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How we model subject matter

J. Šesták

Abstract Modeling tradition is reviewed within its historical maturity from Plato do Penrose. Metaphors in nonisothermal kinetics achieved a wide application mostly employing models derived by means of undemanding isothermal descriptions. Geometrical basis of such modeling is revised and discussed in terms of symmetrical and asymmetrical (pentagonal) schemes. The properties of interface (reaction separating line) are found decisive in all cases of heterogeneous kinetics. Application of fractal geometry is accredited, and associated formal kinetic models based on nonintegral power exponents are acknowledged. Typical erroneous beliefs are dealt with showing common kinetic misinterpretation of measured data and associated mathematical manipulability of kinetic equations. The correction of a measured DTA peak is mentioned assuming the effects of heat inertia and temperature gradients.

Keywords Nonisothermal kinetics · Reaction mechanism · Geometrical modeling · Fractals · Evaluation · Misinterpretation · DTA · Heat inertia

Introduction

More than a quarter century ago, I published in this journal a discussion article on kinetic evaluations [1] emphasizing various questions, which is not worth to repeat even if many of inquires have remained unanswered [2–5]. Since then, many thousands of articles were published showing that the kinetic subject has persisted to be the best cited area in thermal analysis [6]. Albeit being a doyen of such a novel [7–13] and now cross-boundary research area [14], I was proud that I was given yet another space to revaluate and reassume my standpoints toward the thermal analysis kinetics, the subject thoroughly explored in my books [14–19]. Nonetheless, I have decided to do it in a more generalized way pointing out the pitfalls and yet unaccepted site issues to show different ways of possible and untraditional assessments even falling back upon the beliefs of Greek philosophers [18, 19].

Some philosophical thoughts on a general exercise toward mathematical models

The four basic elements fire, air, earth, and water (introduced by Empedocles 492–432) were the first known models and metaphors to signify the substantiality of which all subsistence is composed (i.e., quantities as well as interconnecting qualities like warmness, dryness, coldness, and humidity). They were thought to possess the integrative and structural essence ether or better form in the sense of an imperishable firmament (which in the modern world is interpreted as in-form-ation) [18, 19]. Today however, mathematical modeling ensues differently not only from a further approved physical existence but also from an existence that is assigned by our more cultured mental
perceptions. It is not just the precision but also the subtle sophistication and mathematical beauty of successful models that is profoundly mysterious. Mathematics is crucially concerned about truth and philosophers would agree that there are some other fundamental (almost absolute) concerns, namely that of beauty and of good, which exist since the Platonic geometrical world of mathematical forms [20].

The early modeling elements were first depicted by the metaphors of simple, equilateral triangles either pointing up, in order to escape like air or fire, or down, to rest like water or earth. Later Plato (427–347) used more explicit geometrical models spatially arranging multiple triangles, i.e., 3 triangles formed tetrahedron (~fire), 8 triangles—octahedron (~air), 6 squares or 12 triangles—cube (~earth). Water, however, was represented by a more complex geometrical body called icosahedra (20 triangles, cf. Fig. 1). In Greek culture the term symmetry was interpreted as the harmony of different parts of an object. Symmetria (~common measure) is composed of the prefix sym (~common) and metres (~measure). The Greek Gaius Plinius Secundus (23–79) provided the early fundament for crystallography (derived from Greek cristallos = piece of ice) as he gave primary rules for the plan-metric faces of crystals and their visually imagery shaping.

However, the most impressive historical treatise on crystallography was written by Johann Kepler (1571–1612), while residing in Prague (during 1600–1612), and was devoted to the description of snowflakes. In analyzing their numerous forms bearing a steady hexagonal symmetry, Kepler suggested a certain generalization model for the densest arrangement of rigid balls. Factually, he introduced the coordination-like number for a ball environment and declared the consistency of angles between analogical crystal planes and edges. It can be assumed that some implication of Platonic geometry was also inherent in Kepler’s applications [20]. Though Auguste Bravais (1811–1863) was not sure that crystals are internally arranged in a repeatable manner, he mathematically modeled the 14 geometrical figures which can be spatially arranged in a periodic mode [20–22]. They can be characterized by a combination of one or more rotations and inversions in a lattice that is understood as a regular array of discrete points representing individual structural units (atoms, molecules, species, etc.), which thus appear exactly the same when viewed from any point of the array [20]. This discovery allows us to classify crystal shapes nowadays in the seven geometrically basic schemes: area and/or space can be filled completely and symmetrically with tiles of three, four, and six sides. This is close to the Platonic conceptions of geometrical bodies but excludes, however, any pentagonal arrangement (also involved in the early Platonic bodies) because it is not possible to fill any area completely with its fivefold symmetry. In the early 1970s, however, Roger Penrose (1931–) discovered that a surface can be wholly tiled in an asymmetrical but non-repeating manner [21, 22] providing some constructions similar to the cluster structure of liquid water [23] or glassy state of non-crystalline materials (like metallic glasses), which has been for a long run in the core of attention [19], see Fig. 1.

These relations can be followed far back to history when the geometry of pentagon (and the pentagram inscribed within it) bore its high metaphysical association as explored by the Pythagoreans (after Pythagoras 586–506): they considered it as an emblem of perfection. It was a doctrine that all things compose and proceed from numbers and the middle number five, as being formed by the union of the odd and the first event was deemed of a peculiar value. In China, the central number five, similarly, represented the fifth additional element—the earth as the allied symbol of the great China [18, 19]. In astrology, geometrical figures kept engendering mystical and occult connotations such as with the supposed magical powers of pentagons and pentagrams. This effect lasted until recently as various occult guilds are often symbolized by five leave rose.

One consequence is the way how we fragment real-world entities into several categories [20]: things, events, and processes. By things, we typically mean those entities which are separable, with identifiable shapes and size, and which persist in time. Events, on the other hand, have a relatively short duration and are composed of the interactions of several things of various sizes. Processes are, in this last property, similar to events but, like things, have a relatively long duration. However, many other entities may have a transient character, such as vortices, flames, clouds, sounds, ceremonies, etc. There is an obvious difference between generic categories and particular entities because a category may be scale-thin in two different ways: generically (atoms, birds, etc.) or individually (geometrical concepts, etc.).

In the case of complex objects, there is a close relationship between their distribution over scales and a hierarchy of their structural, functional, and describable levels. We tend to assign objects of our concern into structural levels and events as well as processes into functional levels. Obvious differences of individual levels yield different descriptions, different terminologies (or languages), and eventually different disciplines. Two types of difficulty, however, emerge, one caused by our limited understanding of whether and how distinct levels of a system can directly interact and, the other, related to the communication (words) barriers developed over decades of specialization of scientific disciplines [24] (providing the urgent need for a topic interdisciplinarity).

One of the first mathematical theories in science that dealt with inter-level interactions was Boltzmann’s statistical physics, which is related to thermodynamics and the
study of collective phenomena. It succeeded in eliminating the lower (microscopic) level from the macroscopic laws by decomposing the phase space to what is considered macroscopically relevant subsets and by introducing new concepts, such as the mannered entropy principle. It requested to widely adopt the function of logarithm that was already and perpetually accustomed by nature alone (physiology, and psychology [18]). In comparison, another scaled sphere of a natural process can be mentioned here where the gradual evolution of living parts has been matured and completed in the log/log relations, called the allometric dependence, often penetrating into the kinetic evaluation methods [18, 19, 25].

Another relevant area is the study of order/disorder phenomena [18, 19], acknowledging that microscopically tiny fluctuations can be somewhat “immediately” amplified to a macroscopic scale. What seems to be a purely random event on one level can appear to be deterministically lawful behavior on some other level. Quantum mechanics may serve as an example where the question of measurement is actually the eminent question of interpreting macroscopic images of the quantum-scale events [19]. Factually, we construct “things” on the basis of information; in resemblance we may call engines as information transducers because they transform energy without changing itself (not accounting on wearing).

**Modeling roots applied in reaction kinetics**

In solid-state reaction kinetics [25–40], it is convenient to postulate a thought (gedenken”) model visualizing thus the (Penrose) basic tiles [21, 22] with a specific shape called “rhombus,” where upper thick rhomb has longer diagonal equal to the “Golden ratio” \( \phi = 1.618034 \), which is related to the number 5 by formulae \( 1 - \sqrt{5}/2 \), fascinatingly, playing a crucial role in various aspects of natural livelihood and also man-made art constructions [20]. The thinner rhomb has his shorter diagonal equal to \( 1/\phi \). Both rhombs can be derived from a pentagon, which five diagonals match \( \phi \) and which five-side structure leaves gaps when used to be continuously repeated in space. On the other hand, the rhoms can fill the surface in an asymmetrical and non-repeating manner, which is known as continuous but non-repeating structure (sometimes called quasicrystals). On expanded tiling when covering greater areas, the ratio of the quantity of thick rhombs to thin ones approaches \( \phi \) again, and if the rhombs are marked by shadow strips, then they form the unbroken structure (middle) where we can localize both the chains (like polymers) and pentagons (like water clusters), where the below connectivity map shows the molecules’ orderliness within an icosahedron. Such a structuring can also be applied to a spatial distribution if the two kinds of rhombohedra are assembled to form icosahedrons matching thus the larger clusters (water again), but were never employed in the modeling of reaction solid-state species.
feedback, which is usually separated into a sequence of possible steps then trying to identify the slowest event, which is considered to be the rate-determining process [25]. Such models (among others, e.g., [14, 19, 26–42]) usually incorporate (often rather hypothetical) description of consequent and/or concurrent processes of interfacial chemical reactions and diffusion transport of reactants, which governs the formation of new phase (nucleation) and its consequent (crystal) growth. Such a modeling is often structured within the perception of simplified geometrical bodies, which are responsible to depict the incorporated particles, and such visualization exemplifies the reaction interfaces by *disjointing lines*. Such a derived kinetics then depends on all such physical, chemical, and geometrical events focused to the behavior of interface acting between the product and the initial reactant. Accordingly the space co-ordinates become rate-controlling elements, which create heterogeneity consequence inevitably to be incorporated. At the moment when interfaces are created, they should be identified with the underlying principle of defects conveniently symbolized by a pictographic contour (borderline curves) at our graphical representation (cf Fig. 1).

Hence, the mathematical description turns out to be much more complicated because no *mean measure* (such as bulk concentration and temperature) but the *spot/site/defect assessment* (extent of phase interface or gradients) carries out the *most considerable information* undertaking thus the posture of true rate-controlling process/execute associative with the reaction progress (cf. Fig. 1), not omitting the delivery task of reaction species moving to and/or from reaction boundary.

Early in 1950s, Smith [43, 44] already proposed a classical approach emphasizing “normal grain growth result for the interaction between the topological requirements of space-filing and the geometrical needs of surface tension equilibrium.” We can distinguish that in both 2D and 3D (dimensional) arrangements, the structure consists of vertices joined by edges (sides), which surround faces and in the 3D case, the faces surround cells, see Fig. 1. The cells, faces, edges, and vertices of any cellular structure obey the conservation law (Euler’s equation), i.e., \( F - E + V = 1 \) (for 2D plane) and \( F - E - C + V = 1 \) (for 3D space). Here \( C, E, F, \) and \( V \) are, respectively, the number of cells, edges, faces, and vertices. Moreover, the number of edges joined to a given vertex settles its coordination number, \( z \). For a topologically stable structure, i.e., for those in which the topological properties are unchanged by any small deformation, \( z = 3 \) (for 2D) and \( z = 4 \) (for 3D), is legitimate everywhere. This can be best illustrated for 2D structure by a four-rayed vertex, which will tend to be unstable decomposing into two vertices, each of three-rays, which process is often termed as *neighbor-switching*. For a 2D structure, in which all boundaries have the same surface tension, the equilibrium angels at a vertex are 120°. The tetrahedral angle at 109°28’ is the equilibrium angle at a four-edged vertex in 3D having six 2D faces.

The grain growth in 2D is inevitable unless a structure consists of an absolutely regular array of hexagons. If even 1 five-sided polygon is introduced and balanced by a seven-sided one then the sides of the grains must become *curved* to maintain 120° angles at the vertices. Grain boundary migration then tends to occur because of the curvature maneuver reducing boundary surface tension so that any grain with the number of edges above six will tend to grow because of concave sides and below six will incline to shrink because of convex sides.

It is clear that any reaction rate, particularly at the beginning of its “acting-ion-exchange,” must depend upon the size of the solid grains which undergo transformation (growth or dissolution). Reaction rate, \( r^- \), should thus be inversely proportional to the particle size, \( r \), in the form of a certain power law: \( r^- = r^D_{0.5} \), where \( D_i \) is the *characteristic reaction dimension*, which can be allied with a nonintegral fractal [45–48]. It is obvious that a mere use of strict integral dimensions, typically \( r^3 \) and \( r^2 \), would be an apparent oversimplification. Moreover, we have to imagine that the initial rate is directly proportional to the extent (true availability) of “ready-to-react” surface and/or interface as well as to its coarseness (i.e., roughness as a kind of another characteristic with a non-integral dimension, again). It seems that such a concept can be discriminated as rather useful to describe the responding behavior of a reacting object toward the reaction impact characterized by fractal dimension. It recounts in -self summing all events occurring during the overall heterogeneous process. There, however, is not a regular polyhedron with plane sides subsisting exactly tetrahedral (angle 109°28’ between the edges). The nearest approach to space filling by a regular plane-sided polyhedron in 3D is obtained by the Kelvin ideal tetracaidecahedra spaced on a body-centered cubic lattice. Even then, the boundaries must become curved to assure equilibrium at the vertices so that a grain growth is likely to occur. It can be even illustrated by beer frost, which can be of two kinds: at-once draft beer with more interfacial fluid possessions (enabling mutual bubble slipping) and the already aged beer with a more rigid interfacial structure (~“dry” hexagonal-like make up). Apparently, both are unlike in experts’ taste, being capable, however, to self-adjust by boundary migration and gas permeation through the cell membranes to equalize pressure of adjacent bubbles.

The most common kinetic models are associated with the shrinking core of a globular particle, which maintains a *sharp* reaction boundary [26–36]. Using a simple geometrical representation, the reacting system can be classified as a set of spheres [18, 19] where each reaction interface is
represented by characteristic curve. We assume that the initial reactants’ aggregation must be reached by (assumingly) well-distributed (homogenization of reacting) components (often through various transporting means) otherwise possibly initiating certain self-organization [18, 19]. Any of such created interfacial (separating) layers, y, endures thus the role of a kinetic impedance, and the slower of the two associated elementary processes, i.e., diffusion to/ from acting along with the chemical interface, then becomes the rate-controlling process [18–42, 49–51] responsible for the over-all reaction progression. We may indicate that that the above discussed kind of “as-belief” models depict both the ideal situation of only single-reaction controlling mode as well as a rigid spherical representation for all reacting particles. Though this simplification has no any investigational authorization, such a theoretical fashion sometimes (and from time to time even routinely) provides a surprisingly good fitting for thermoanalytical data kinetics ignoring a common inspection misfit often adjusted by means of simultaneously achieved direct observations (such as microscopy). Rationalized approach can be accomplished when assuming a certain model coincidence for improved geometrical fit incorporating thus some additional symmetry features such as a regularity adjustment of pattern-similar-bodies (globe → prism → cube → block → hexahedral → dodecahedral → etc.). It somehow helps us to authorize the relation truthfulness and applicability of such (oversimplified) models when put into operation on more cogent (irregular) structures, which we often decline, or at least, are anxious to observe. Even symmetry generalization does not facilitate above modeling to the full-scale matching of real morphologies (customarily witnessed in practice).

In our kinetic practice, we can either survive with a simplified model-free description using a “blank” modeling pattern (as below shown SB equation) or we ought to adapt another philosophy of modeling whichever reaction mechanisms, learning how to employ more complex mathematics and/or providing a range of functions instead of simple numerical values (typically activation energies often pointlessly précised to decimal places). This tactic, however, may auxiliary interfere within the limiting cases of experimental setup: either by diminishing the sample size to a certain threshold (thus being incapable of distinguishing the measured response of bulk behavior from that of sample surface) or by accelerating the imposed temperature changes (≫ϕ) probably getting in touch with an effect analogous to the uncertainty principle (unable to correspondingly determine each one of the independently measured parameters with an adequate precision, i.e., temperature and/or and its change—heat flux). Therefore, the future development of thermal analysis may become different than that we presuppose today.

Use of yet atypical fractal geometry

Always existing perturbations on the reaction interface can be imagined to encounter a driving force to accelerate growth that is usually expressed by the negative value of the first derivative of the Gibbs energy change, ∆G, with respect to the distance, r. For small super-heating/cooling, we can still adopt the concept of constancy of the first derivatives, so that d∆G equals to the product of the entropy change, ∆S, and the temperature gradient, ∆T, which is the difference between the thermodynamic temperature gradient (associated with transformation) and the heat-imposed gradient at the reaction interface as a consequence of external and internal heat fluxes. Because ∆S is often negative, a positive driving force will exist to allow perturbations to grow, only if ∆T is positive. This pseudo-thermodynamic approach gives the same result as that deduced from the concept of zone constitutional undercooling [52, 53], and its analysis is important for the manufacturing advanced nano-materials [54–57] such as fine-metals, nano-composed assets, formation of quantum low-dimensional possessions (dots), composite whiskers, tailored textured configurations, and growth of oriented biological structures.

The physical–geometrical models also neglect other important factors such as interfacial energy (immediate curvature, capillarity, tensions, nano-grains radius [54–57]), and particularly undistinguish internal and external transports of heat and mass (to and from the localized reaction boundary) resulting in a breakdown of smooth (planar) reacting interface [19], which, at the process terminations, are anyhow responsible for complex product topology [52, 53]. Variously activated disturbances are often amplified until a marked difference in the progress of the tips and depressions of the perturbed reacting interface occurs, making the image of resultant structures irregular and indistinguishable [19, 52–54, 58]. It creates difficulties in the correlation of traditional morphology observations with anticipated structures, becoming rather different from the originally assumed (simple, planar, 3D, etc.) geometry. Depending on the directional growth conditions, the so-called dendrites (from the Greek dendros = tree) develop their arms of various orders and trunks of different spacings because of the locally uneven conditions of heat supply. This process is well known in not only metallurgy (quenching and casting of alloys [52, 53, 58], water, and weather precipitates (such as snow-flakes formation or crystallization of water in plants) but also for less frequent types of other precipitation, crystallization, and decomposition processes associated with dissipation of heat, fluids, etc.

First, we should notice that there are sometimes fussy effects of particle radius, r, encompassing a wide range of
reacting compacts. Besides affecting measurable point of phase changes [55–57], the most of the derived model relations stay either for a simply reciprocity (∼1/r, if the whole reacting surface is exposed to ongoing chemical events) or for the inversely proportional square (∼1/r², if the diffusion across the changing width of reactant/product layer became decisive). It is clear that for a real instance, we can imagine such a situation when neither of these two limiting cases is unfalling so that the relation 1/rⁿ becomes effective, and a new non-integral power exponent, n, comes into view falling to the fractal region 1 ≤ n ≤ 2. It is somehow similar to the case of heat transfer across the layer d, which can similarly fall in between two optimal cases limited by 1/d and 1/d². The associated cooling rate φ is essentially influenced by the heat transfer coefficient, Λ, and the thickness of cooled sample, d, and relatively less by its actual temperature, T. At the condition of ideal cooling, where we assume infinitely high coefficient of heat transfer, the cooling rate is proportional to 1/d², while for the Newtonian cooling controlled by the character of phase boundary, φ correlates to 1/d, only. In practice, we may adopt the power relation φ = 1/dⁿ (where n is a nonintegral experimental constant 1 ≤ n ≤ 2).

We can presuppose that transport properties, because of fractal nature of percolation changes, incorporate into the physical laws. For an enough randomly diluted system, we can even admit that the localized modes occur for larger reacting frequencies, which can be introduced on basis of bizarrely called fractions [18, 59]. Inherent state density then shows an anomalous frequency behavior and, again, the power laws can characterize their dynamic properties. On fractal conductors, for example, the density is proportional to L² and approaches zero for L → ∞. If we increase L, we increase the size of the non-conducting holes, at the same time decreasing the conductivity, σ, which, because of self-similarity, decreases on all length scales, leading to the power law dependence defining the critical exponent, μ, as σ ∼ L⁻μ. Owing to the presence of holes, bottlenecks, and dangling ends, the diffusion is also slowed down on all length scales. Assuming the common example of “random walker” [60–63] and its probability to stay in place (using the standard relation, x²(t) = 2Dt, where D is the diffusion constant and d is the dimension of lattice), the classical Fick Law loses its orthodox validity. Instead, the mean square displacement is described by more general power law: x²(t) ≃ t²/dₓ, where the new exponent, dₓ, is always greater than two. Both exponents can be related through the Einstein relation, σ = e n D/k_BT, where e and n denote, respectively, the charge and density of mobile particles, and k_B is a rate constant. As a result, dₓ = d′ − d + 2 + μ, where d′ can be substituted by the ratio relation, log3/log2, so that dₓ becomes proportional to log5/log2, which, however, is not so easy to ascertain in the standard integer-like cases.

It is widely shown [60–63] that many dynamic systems can regularly produce a chaotic behavior. One set of associated problems for us is the investigative concern in the direction of a difference equation called logistic mapping obviously being the quadratic transformation, which comes in different forms, typical succession as x → a x(1 − x). This name sounds a little peculiar in modern science as its origin subsisted in economics from which it gives us the term logistic to describe any type of a planning process. It derives from the consideration of a whole class of problems in which these two factors control the size of a changing population, x varying between 0 and 1. This population passes through a succession of generations, labeled by the suffix n, and so we denote the population in the nth generation by x_n. There is a birth process in which the number of populated species (nuclei, insects, and even people) would deplete resources, and prevent survival of them all. There is a negative depletion term proportional to the square of the population. Putting these together, we have the nonlinear difference equation. By defining the iteration as x_{n+1} = a x_n(1 − x_n), we can illustrate the process graphically upon the superimposed parabola (x²) and straight line (x) in the interval 0 ≤ x ≤ 1 [18]. We can arrive to the two types of iterations by adjusting both the initial point, x₀, and the multiplying coefficient, a. It can either exhibit a sensitive-irregular pattern or non-sensitively stable behavior. Very important phenomenon is thus sensitivity, which either can magnify even the smallest error or dump the larger errors, if the system is finally localized in the stable state. This behavior is called the sensitive dependence on initial conditions and is central to the problematic of chaos [18, 49, 60–63], though it does not automatically lead to disorder.

The crucial difference between the discrete logistic system and its continuous derivative-like counterpart subsists in the fact that it is plainly impossible for the dynamics of the differential equation to behave chaotic. The reason is that in the 1D system, no two trajectories, for the limit Δt → 0, can cross each other, thus typically converging to a point or escaping to infinity, which, however, is not a general consensus in 3D system often displaying chaos. These types of differential equations are the most important tools for modeling straightforward (“vector”) processes in physics and chemistry, though, no single particular analytic solution is regularly available. The associated relationship can be transposable to write the form of a common kinetic equation: dz/dt ≃ a(1 − z), where z can be the normalized extent of chemical conversion. Factually, this is a well-known form of Prout-Tompkins’ self-catalyzed kinetic model [64, 65] naturally.
related to various aspects of contradictory chemical reactivity. However, life in the real science is not simple and almost in any physical–chemical system, the state cannot be described by a single variable or equation characterized by an integral power exponent \((=1)\), as shown in detail in the previous paragraph. Therefore, it was obvious that for generalized purposes of chemical kinetics, this logistic-like approach to inaugurate the desired constitutive equation \([73, 75]\) depicts a principal form of the product of two separate functions, i.e., the rate constant \(k(T)\), dependent solely on the temperature, \(T\), and the mathematical portrayal-model of the reaction mechanism \(f(z)\), reliant on the variation of the degree of conversion, only \([18, 19, 74]\). It may be complicated by interference of a changing equilibrium background in which \(z\) became a product of two kinetic \(\dot{z}\) and equilibrium \(z_{eq}\) degrees \([75]\) \((z = \dot{z}/z_{eq})\). The degree of conversion may eventually involve multiple kinetic degrees (such as simultaneous phase separation \([76]\) etc.) and may also become pressure dependent, etc.

For a mathematical treatment, we have any number of possibilities of mathematical manipulations: we can adjust modification of either term: \(dz/dt \sim \dot{z}'\), \(f(z)\) or \(k(T)\). We are all familiar that the derivative can possess only an integer order \((1, 2, 3 \ldots)\), which is a common language for formulating and analyzing many laws of physics. In accordance with above discussion, even the calculus of fractional derivatives \([77, 78]\) may become adequate to be employed for kinetic applications (factually being an old technique selected by Gottfried von Leibnitz already in 1695), i.e., \(dx^n/dt^r\) (explicitly for a case of \(x = \dot{1}/2\) it makes equal to \(\dot{z}/(dz/\dot{z})\) \([77, 78]\)). It has already affected the classically derived Fick law of diffusion, showing certain exceptions, which is termed as a strange kinetics \([79]\). It is based on the portrayal of a random walker concept (see above) and on an unconventional distribution of functions. In standard kinetics, however, fractional derivatives did not come into sight as yet which does not exclude a chance that in future a mathematically based application would surface conquering its apparent controversy embedded nowadays. Worth noting is another curiosity associated with derivatives, which appeared when the constitutive rate \(dz/dt\) was incorrectly treated as a multiple of two partial terms, i.e., temperature \((dz/dt)_{T}\) and time \((dz/dt)\), dependent \([2, 3, 73–75]\). This implication created a long-lasting anarchy in the scientific literature fortunately clarified in time \([18, 19, 73]\) though some strange commentary issues keeps persistent until today.

A long-lasting kinetic practice employs both functions \(k(T)\) and \(f(z)\) after their analytic implementation. Traditional approach habitually employs the Arrhenius exponential constant because kineticists believes \([19, 80, 81]\) in the exponential law of energy distribution, \(k(T) = A \exp (-E/RT)\), derived by Arrhenius for the stochastic process of evaporation (and approved by Boltzmann statistics). However, experimentalists often think it can be proved mathematically while the mathematicians believe it has been established by observations. Parameter \(E\) is the so-called activation energy identified as the energy barrier (or threshold) that must be surmounted to enable the occurrence of the bond redistribution steps required to convert reactants to products. The pre-exponential term, or frequency factor,
A, provides a measure of the frequency of occurrence of the reaction situation. Although the Arrhenius equation has been widely (and often successfully) applied to innumerable solid-state reactions, its use factually lacks a theoretical justification (merely acknowledged in homogeneous systems) because the energy distribution, particularly among the immobilized constituents of crystalline reactants, may not be adequately represented by the Maxwell–Boltzmann equation. The interracially reacting species, however, encompass a certain degree of freedom to adjust their energy distribution along the surface reaction zone affecting the energy sharing in reactive sites (reaction interfacial contact), moreover exaggerated by strain (between the differently juxtaposed networks), nonstoichiometry, defects, catalytic activity of newborn sites, irreversible re-crystallization, or perhaps even by local volatilization (if not accounting for the thickness of such a reacting zone contoured by local heat and mass fluxes across and along the interfaces). An alternative framework for this theory of solid-state decompositions [82] is available through the so-called L’vov’s [83] congruent dissociative vaporization (CDV) mechanism. Here the super-saturation (S) of the vapor of the low-volatility component at the instant of decomposition is related through a transfer parameter \( \tau \) by proportionality (\( \tau \approx 0.351 \) log log S + 0.017). However, this unusual (doubly logarithmic) relationship between \( \tau \) and S may become a key point in understanding the mechanism of energy transfer in condensation (for low volatility component distribution between reactant and product solids) depending on the ratio characterized by the \( \tau \)-coefficient.

When \( f(x) \) function is routinely modeled on basis of simplified physical–geometrical assumptions [14–19, 25–42], the direct application of the basic differential equation is straightforward. However, the differential mode of evaluation can even provide a better matching up with the true experimental conditions when the actual non-uniform heating and factual temperatures are considered. In such a case, we ought to introduce the second derivatives, \( T'' \) and \( x'' \) leading to a more complex equation correlating \( z''T''/z'T' \) with \( df(x)/dx/f(x) \{T^2/z'T'\} + \exp EA/R \). It occurs that it is almost impossible to evaluate this relation with a satisfactory precision because of its extreme sensitivity to noise, particularly affecting the second derivatives (as well as heat flow changes, \( q'' \), see below) A more convenient and rather popular method of kinetic data analysis is based on expressing the maximum value (index \( \max \)) on the dependence of \( x' \) versus \( T \), for which it holds, \( x'' = 0 = x'' \max \{E/R \max \phi \exp (-E/R \max) \} df(x)/dx \). The result provides simple but rather useful dependence, often called Kissinger plot (known since 1959 [84]), which in various modifications and reproves shows the basic relation between the ratio of heating rate \( \phi \) and the peak maximum temperature \( T_m \) along with the activation energy \( E \).

The so-called integral methods of evaluation [14, 18, 19] have become recently more widespread. They are based on a modified, integrated form of the function \( f(x) \), which is determined by the following relation, \( g(x) = \int_0^x dx / f'(x) \) and rather intricate integration of the rate constant \( \int_0^2 k(T)dT/ \phi = (AE)/(\phi R) \exp (-E/RT) \pi(x)/x \) where \( \phi \) is the constant heating rate applied, \( \pi(x) \) is an approximation term of the temperature integral (a common target of numerous publications [42, 85]). In many cases its value is simplified and even neglected, which can be visualized by simple withdrawal in front of the integral, namely: constant \( \int k(T)dt \approx k(T) \int dt \). This mathematical handling is habitually obscured within complicated mathematics but got involved in the nonisothermal derivation mode of traditional nucleation-growth (JMAYK) equations [76, 86, 87].

It is evident that the derivation increases discrimination introducing, however, too high sensitivity to experimental noise and, on contrary, the integration decreases noise sensitivity but launches a lower indifference toward different \( f(x) \)-resolution (discriminability) [18, 19]. In the history of kinetic appraisal, there appeared curiosity when three similar but also disparate ways of evaluation seeks for a linear correlation of the logarithmic form of kinetic model function \( \ln g(x) \) either \( \ln T \), \( 1/T \) and \( 1/T \); all making available a equivalent outlook for the corresponding values of activation energies, \( E \), evaluated from the slope of respective plots. Such an inbuilt disparity is caused by the different approximation of \( \pi(x) \) function applied differing in the multiplication parameter, which by itself well indicates a certain extent of inherent inexactness of such a kind of kinetic evaluation. A better insight of this inquisitiveness was provided by the use of an asymptotic expansion [88] of a series with a dimensionless parameter replacing \( E_{app} \). It revealed that the \( \ln g(x) \) versus \( 1/T \) plot is twice as good as that of the former two dependencies. In this way, we can also substantiate the numerical results of several authors who found that the plain dependence of \( \ln g(x) \) versus \( T \) yields \( E \) with an error of at least 15%, whereas the \( 1/T \) plot can decrease this error by half.

Important practical correlations were adjusted for variously interpreted \( E \) [15, 19]. For example, a rather sophisticated correlation provides interrelation between the experimental activation energy, \( E_{DSTA} \), and those for shear viscosity, \( E_p \), on the basis of the relative constant width of glass formation interval, \( T_g \) (i.e., difference between the onset and outset temperatures). It reveals a rough temperature dependence of the logarithm of shear viscosity \( \eta \) on the measured temperature, \( T \), using the simple relation log \( \eta = 11.3 + \{4.8/2.3 \Delta(1/T_g)\}(1/T - 1/T_g) \) [89] detailed discussion of which is beyond the scope of this text.

The basic JMAYK equation reveals that the apparent (overall) values of activation energies, \( E_{app} \) (particularly
being the center of interest when determined on the basis of DTA/DSC measurements, \( E_{\text{DTA}} \) can be conveniently correlated to the partial activation energies \([14, 18, 19, 42, 90, 91] \) of nucleation, \( E_N \), growth, \( E_G \), and/or diffusion, \( E_D \) employing a simple relation \( E_{\text{app}} = (a E_N + b E_G) / (a + b d) \) where \( a \) and \( b \) are characteristic multiplying constants providing that the denominator \((a + b d)\) equals to the robust power exponent of the integral form of JMAYK equation \([18, 19, 71, 72] \), and the value \( b \) corresponds to \( 1 \) or \( 1/2 \) related to the movement of growth front controlled by either chemical reaction \( (1) \) or diffusion \( (1/2) \). Moreover, the coefficients \( d \) and \( b \) are associative with the nucleation velocity and the growth dimension, respectively. I am proud to mention that I was the first person pointing out such a likelihood \([90] \), though it may become a persuasive but often misleading tool in an effortless interpretation of reaction mechanism.

The above evaluation quandary can be eased upon the application of the sample controlled thermal analysis (SCTA) method or constant rate thermal analysis (CRTA), where it is not monitoring the constant increase of temperature but the constant rate of reaction \( (\dot{x} = dx/dt \text{ constant}) \) [92–94]. It, however, does not help in avoiding undesired mathematical interrelation between the pre-exponential factor \( A \) and the activation energy \( E \) in the standard exponential law (the so-called kinetic compensation effect—KCE) [95–98]. A complementary help can be achieved when employing simultaneous experimental techniques such as optical microscopy [99–101] or dilatometry [100, 101].

Only plausible aid is introducing a novel kind of rate constant [102] or treating the kinetics in the novel so-called model-free or nonparametric mod of evaluation [103–106] where the traditional functions \( k(T) \) and \( f(x) \) are replaced by a joint function \( f(x, T) \), thus going back to the roots of kinetic evaluations. It may avoid customary exploitation in terms of ill-reputed and almost religious constants, mostly linked with the activation energies that never express the reaction progress (to be desirably related to the reactivity as a kind of “tolerance” and to the reaction mechanism as a kind of “annexation”).

In conclusion, I would like to draw attention to yet other outstanding issues that we outlined 40 years ago when interpreting a compositional case of a measured DTA peak assuming the inherent effect of heat inertia [107–110] (i.e., the term \( d\Delta T_{\text{DTA}} / dr \) which is a standard part of the DTA and/or heat-flux-DSC equation \([14, 19, 107, 108, 110] \)). Such an expediency rather of great importance has remained overlooked in most books \([30, 31, 112–114] \) (with few exceptions \([18, 19, 115] \)). Our recent studies \([111] \) indicate that this feature is not a fiction but bears a true consequential impact arising from the real process of heat transfer \( (q) \) which has the greatest impact for moments where the heat flux is immediately changed \( (<<q) \). Our numerical stimulations [111] show that the heat inertia effect is even amplified because of such temperature gradients affecting thus the shape of corrected DTA peak. Associated mistakenness is not reduced by shrinking the sample size to micro-level [111]. It is questionable whether such difference between the measured (as-determined) and authentic (as-rectified) DTA peak impinging on the supplementary derived data especially when calculating the reaction progress \( (x) \) from the enveloped peak areas and/or on the kinetic data evaluated from the shift of peak apexes [84] or fractionally determined at successive \( x \)'s. It is an open sphere for further examination and DTA evaluation scrutiny together with hidden and yet unidentified problems [111] brought about by lessening the sample micro-size [19, 55–57] and escalating the employed heating/cooling rates [19, 52–54].

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STUDY OF THE KINETICS OF THE MECHANISM OF SOLID-STATE REACTIONS AT INCREASING TEMPERATURES

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ABSTRACT

Possible reasons for the misinterpretation of non-isothermal kinetics are discussed. The importance of the correct selection for the assessment of the progress of the reaction and the acquisition of representative experimental data, as well as the effect of non-isothermal conditions and possible change of the equilibrium on the kinetic equation are stressed. Detailed attention is given to the probable mechanisms of individual cases of solid-state reactions as expressed in integral and/or differential forms of kinetic equations. Reactions controlled by the movement of phase boundaries, by simple nucleation, by nucleation followed by nuclei growth and by diffusion are discussed; a combined form of differential equation suggested for the preliminary appraisal of possible mechanisms is

\[
\frac{d\alpha}{dt} = k\alpha^n(1-\alpha)^p(-\ln(1-\alpha))^p
\]

INTRODUCTION

The study of reaction kinetics in the solid state (and/or liquids) is mainly designed to gain information about the kinetic parameters and associated mechanisms of the process. In dynamic experiments with increasing temperature\(^1\)–\(^4\)

\[
\frac{dT}{dt} = \Phi \quad \text{and} \quad t = \frac{T-T_0}{\Phi}
\]

where \(\Phi\) is the linear heating rate and \(T_0\) the temperature of the equilibrium of conversion\(^5\), the calculation of kinetic parameters is often simplified and may be based on the assumption that the course of the reaction can be described by the differential equation

\[
\frac{d\alpha}{dt} = k'(T)f(\alpha)
\]

where \(\alpha\) is the degree of conversion, \(d\alpha/dt\) the rate of reaction, \(k'(T)\) the temperature...
dependent rate constant and $f(z)$ a function* which represents the hypothetical model of the reaction mechanism. Apart from direct investigational methods$^{9,32,33}$, mathematical models based on hypothetical reaction mechanisms may be used$^{7,8,33-53}$.

The correlation between the reacted fraction ($z$) and time of reaction ($t$) is usually derived for isothermal studies and the variables are given in a complex form

$$z = f(V, N, \theta, r, p, t \ldots)_{T=\text{const.}}$$

where

- $V$ = reacting volume of material
- $N$ = number of nuclei (or spots available for nucleation)
- $\theta$ = specific surface
- $r$ = geometric factor of particles (radius etc.)
- $p$ = partial pressure of the gaseous products

### POSSIBLE SOURCES OF ERRORS AND MISINTERPRETATIONS IN NON-ISOTHERMAL KINETICS

#### a. Selection of a correct expression for the degree of reaction

Contrary to gases (or liquids), concentration is not a valid representative parameter for solid-state processes as it may vary through the sample$^3$. Therefore, a nondimensional term, degree of conversion $z$, should be introduced. The problem is, in what sense is the value of $z$ a linear function of the physical property measured$^6$ and how does it represent the state of the system investigated. In basic thermoanalytical methods, such as thermogravimetry (and dilatometry) this function is defined as

$$z = \frac{V_t - V_0}{V_{\infty} - V_0} = \frac{W_t}{W_{\infty}}$$

where $V$ and $W$ are weight (volume) and weight loss (volume contraction) of the sample, and indexes 0, $t$ and $\infty$ indicate initial, instantaneous and final stages, respectively. Differential thermal analysis is still of questionable validity$^{31}$ because a representative value which would unambiguously define the change in the system from the initial or from the final state is not yet available from a DTA peak.

#### b. Selection of the experimental condition for a representative experimental process model

All variable factors describing experimental conditions, such as grain size distribution, sample packing and geometry as well as the effect of dynamic environ-

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* $f(z)$ is frequently oversimplified as $(1 - z)^n$ or $z^n$ assuming analogy with homogeneous kinetics of gases$^{1-4}$, and setting $n$ and $m$ as orders of reaction. This simplification has, however, no general validity for solid-state reactions$^5$ but as an approximation it may be used to investigate the variation of apparent activation energy under different experimental conditions$^{29}$. 
SOLID-STATE REACTIONS AT INCREASING TEMPERATURE

ment and vacuum, should be defined in terms of the equilibrium of the process and be included in the function \( f(z) \) if they alter the reaction mechanism. Temperature deviation from a chosen temperature increase (e.g. due to heat of reaction in the sample) should be minimized. Uniform and programmed temperature throughout the sample body is required for the successful kinetic investigation of solid state reactions. Heat and mass transport should be facilitated as much as possible by a suitable experimental arrangement, unless they are true and valid rate controlling processes.

Two possible approaches when investigating solid-state processes can be distinguished. The physicochemical approach is to separate and stress that process usually associated with the re-arrangement of molecules and ions when forming a new phase. Specially developed experimental conditions are applied (e.g. thin layers of solid samples in good contact with large heat reservoirs) in order to obtain information about the nature of physical and/or chemical changes. On the other hand, the engineering approach is used to analyse the experiments (employing large solid samples with well defined outer geometry) in terms of thermal and concentration gradients in order to obtain information about the practical application of the process.

c. Admitting a continuous change of the equilibrium of the process during temperature increases

Contrary to the invariant processes, where the equilibrium state of the system changes by a jump, in monovariant processes equilibrium can be a monotonous function of temperature within the temperature interval of the reaction. Therefore a non-isothermal degree of conversion \( \lambda \) should be introduced

\[
\dot{\lambda} = \alpha \dot{\lambda}_{eq}
\]  

where \( \dot{\lambda}_{eq} \) is the propagation of the equilibrium. The ordinary rate of reaction \( d\lambda/dt \) must then be replaced by the corrected rate of the process \( d\dot{\lambda}/dt \)

\[
\frac{d\xi}{dt} = \left( \frac{d\dot{\lambda}}{dt} + \dot{\lambda} \frac{d \ln \dot{\lambda}_{eq}}{dT} \right)/\dot{\lambda}_{eq}
\]  

Thus it is necessary to establish the dependence of \( \dot{\lambda}_{eq} \) on \( T \).

d. Construction of a kinetic equation of solid-state reactions under non-isothermal conditions

There are some doubts as to the validity of the currently used kinetic equation (Eqn. (2)) either when describing heterogeneous and/or solid-state reactions or when considering the non-isothermal character of processes.

It is the total concept of the specified rate constant (Eqn. (2)), frequently expressed in the form of the Arrhenius equation.

\[
k(T) = A \exp\left(-E/RT\right)
\]  

which has been successfully employed and derived for homogeneous kinetics. $A$ is the frequency factor proportional to the number of successful collisions of the reacting molecules and $E$ is the activation energy. Polanyi and Wigner attempted a quantitative treatment of the rate of solid state reactions using $k(T)$ (Eqn. (7)). They assumed that the molecules which achieved the critical energy $E$ could escape from the reactant surface (here $A$ is the atomic frequency of vibration).

Generally the exponential character of the rate constant for solid state reactions can be accepted, as all true solid state processes are activated processes. The rate constant represents the statistical probability for the energy barrier $E$ to be surpassed when the system undergoes an effort with sufficient activation energy ($E$). The pre-exponential factor $A$ can then be correlated with the number of successful attempts. The missing term $T^m$ for multiplying $A$ (where $0 < m < 1$ is derived in different ways depending on the theoretical application of $k(T)$) can be neglected when working in narrow temperature intervals, and included in $A$ (together with the initial weight and the molecular weight of the sample).

For a particular analysis of solid state reactions as applied to the thermal decomposition of carbonates, the activated complex theory has been employed. $A$ in Eqn. (7) is then proportional to the Maxwell distribution coefficient $kT/h$ and the ratio $Q^*/Q$, where $Q^*$ and $Q$ are complete partition functions for the activated complex and reactant, respectively. The partition function can be expressed using the partial partition function for translation, rotation and vibration for each unit of the crystal lattice undergoing the change, with regard to their possible activities. A good agreement between experimentally calculated and numerically predicted rate constants for various types of decompositions has been found.

A recent publication claims that the current state of knowledge of solid state kinetics is inadequate. New assumptions are made, namely that heterogeneous reactions are not activated processes (with no activation energy) and that the only rate controlling process is heat exchange between the reacting mass and its surroundings.

Furthermore, it is suggested that the reaction can proceed only at a fixed (reaction) temperature $T_R$, given by the equilibrium of the process (where the free enthalpy $\Delta G = 0$). The corrected rate constant is then found to be proportional to the heating rate, transfer of heat (heat conductivity) and to the reciprocal value of the heat of reaction. Good agreement is found for several types of endothermic decomposition.

The objection is, however, that in this case the physical property chosen (e.g., weight) for measuring reaction advancement is controlled by a heat supply corresponding to the instantaneous thermodynamical need for the interface reaction equilibrium ($T_R$ at $\Delta G = 0$). This becomes true for specific conditions of voluminous samples, where the progress of reaction is governed by the interface advancement (or crystal growth in certain cases), as will be considered in the next section. In other cases activated types of process which can proceed at temperatures higher than $T_R$
can also be accepted (where $\Delta G < 0$), but no proof is yet available for either of these assumptions (by measuring and distinguishing whether the reaction proceeds at $T_R$ or above $T_R$).

Another source of doubt is the time-temperature dependence of $x$ under non-isothermal conditions.

$$x = f(t, T(t))$$

(8)

In accordance with established mathematical rules for partial derivation, Eqn. (8) can be rewritten as

$$\frac{dx}{dt} = \left( \frac{\partial x}{\partial t} \right)_T + \left( \frac{\partial x}{\partial T} \right)_t \frac{dT}{dt}$$

(9)

Some authors\textsuperscript{1,2,19} claim that the formal isothermal kinetic equation is valid in the form

$$\left( \frac{\partial x}{\partial t} \right)_T = k(T) f(x)$$

(10)

contrary to the current formulation of Eqn. (2). Using pure mathematical operations, the combination of Eqns. (9) and (10) results in the corrected non-isothermal rate constant $k'(T)$ in the form\textsuperscript{6}

$$k'(T) = k(T) \left( 1 + \frac{T - T_0}{T^2} \frac{E}{R} \right)$$

(11)

This correction is calculated to give $\pm 50\%$ in $E$ for $(T - T_0) < 10$ and $E < 10^4$. Although it is difficult to imagine the physical meaning of the change of the degree of conversion with temperature when time is kept constant\textsuperscript{11}, particularly when temperature can change within a definite time interval, isochrones ($t = \text{const}$.) can be drawn\textsuperscript{19}. This, in its way a mathematically correct approach needs more examination as there is little experimental evidence as well as logical justification\textsuperscript{5}.

There is still a confusing deviation in the activation energy values calculated from data derived from the first part of experimental results of the process. If probable experimental errors are neglected, the best mathematical approach seems to be the appreciation of a correction for the proximity to equilibrium\textsuperscript{13,18}

$$k'(T) = k(T)(1 - \exp(-\Delta G/RT))$$

(12)

where the change of free energy for the reaction ($\Delta G$) approaches zero at the equilibrium temperature $T_0(\exp(-\Delta G/RT_0) \rightarrow 1)$ and is unchanged for stages distant from equilibrium ($\Delta G \ll 0$).

This correction has a logical justification in the obvious "activation energy" diagram, $\Delta G$ vs. reaction travel, and can also be derived by means of irreversible thermodynamics. The expression was originally derived for transformations passing through the vapour phase\textsuperscript{13}, and satisfactorily applied to describe heterogeneous kinetics.

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It must be admitted that the theoretical concept of $k'(T)$ for solid state reactions studied under non-isothermal conditions is still not satisfactorily resolved, but it is difficult to believe that a new concept will be introduced. The proportionality constant ($K \equiv$ integral form, $k \equiv$ derivative form) in the next section will, however, be used without a closely defined meaning.

\[ \text{e. Physical meaning of evaluated kinetic parameters} \]

Many theories have been advanced\textsuperscript{7,8,21,22,38} in order to give a true meaning to the pre-exponential constant $A$ (see Eqn. (2)). Generally it can be said that $A$ can include many constants describing the initial state of the sample, such as three-dimensional shape factors of initial particles, molecular mass, density, stoichiometric factors of chemical reaction, active surface and number of lattice imperfections, \textit{etc.}, as well as factors arising from the surface adsorption of gas, and pressure.

The activation energy $E$ can be understood only in relation to the rate controlling processes. For example, in the case of diffusion, $E$ can be associated with the activation energy of intrinsic diffusion as well as for substitutitional reactions. Proportionality between $k(T)$ and the specific electronic conductivity can be established by the activation energy of electrical conductivity. Also, for nucleation and crystal growth the value of $E$ is composed of activation energies of mass supply (diffusion) and factors arising from the thermodynamical potential of nucleation and/or crystal growth, \textit{etc.}

\[ \text{f. Construction of a hypothetical mathematical description of the reaction mechanism} \]

A formal equation in general use (similar to Eqn. (2)) and applicable to solid-state reactions should represent the relation between $dz/dt$ and $z$. It sometimes includes a term $f(z)$ as well. This type of differential equation implies pure mathematical fitting of experimental data and may be treated in two ways:

1. As a pure mathematical fitting of a polynomial to the experimental curve, the expression

$\hat{f}(z) = A_0 + A_1 z + A_2 z^2 + \ldots \ldots + A_n z^n$ \hfill (13)

is usually employed in computer calculations of mathematical derivations (process rates)\textsuperscript{28-30}, without considering the specific reaction mechanism. Also, the use of the term "reaction order"\textsuperscript{3} is included, having a certain physical and engineering application.

2. By using a certain logical model to form the function $f(z)$ in accordance with the suggested reaction mechanism.

This equation includes the basic geometrical and physicochemical aspects of processes. A detailed analysis of this problem for classifying final equations in a simplified way is the aim of this article and will be dealt with in the following section (all thermodynamically directed aspects discussed in this section were given in detail in a previous article "Kinetics with regard to the thermodynamics of processes studied by use of non-isothermal techniques"\textsuperscript{6}).
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MATHEMATICAL DESCRIPTION OF POSSIBLE MECHANISMS IN SOLID-STATE PROCESSES

The reaction mechanism can be expressed in two ways. The ordinary formulation \( z \times t \) as employed for basic isothermal concepts (see Eqn. (3))7-9,32-50 is here mathematically transferred into the relation \( \frac{dz}{dt} \times z \) in accordance with the requirement given by the differential Eqn. (2)3,4,10. The final and simplified forms of formal kinetic equations are listed below for individual types of mechanism. The left-hand side presents the equations frequently called the integrated form15-18 and provided with function \( g(z) \). These functions14-19 were satisfactorily employed in the only known method for the estimation of reaction mechanisms from dynamic TG traces by using monograms17-10. The right-hand side gives the equivalent forms of the function \( f(z) \).

a. Phase-boundary controlled processes

Surface nucleation takes place extremely rapidly and the total process is governed by movement of the resulting interface towards the center.7,39

A. One-dimensional movement (and some cases of evaporation)2-2

\[ z = Kt; \quad \frac{dz}{dt} = kx^0 = \text{constant} \]  

B. Two-dimensional movement (for cylinder or prism)

\[ 1 - (1 - z)^{1/2} = Kt; \quad \frac{dz}{dt} = k(1 - z)^{1/2} \]  

C. A sphere reacting from all surfaces inwards (three-dimensional movement)

\[ 1 - (1 - z)^{1/3} = Kt; \quad \frac{dz}{dt} = k(1 - z)^{2/3} \]

b. Reactions controlled by nucleation

A. Nucleation according to the power law7,8

\[ z = Kt^p; \quad \frac{dz}{dt} = kx^m \]  

where \( m < 1 \) and \( p = 1, 2, 3, 4 \) according to the spherical symmetry36 of nuclei.

*The rate controlling process might be the chemical reaction on this interface as given by Eqns. (14), (15), (16) or the mass and/or heat transport to or from this surface, such as diffusion or heat exchange19 as a special case of a non-activated process following the equation19,20:

\[ 1 - (1 - z)^{1/3} = K_0 \frac{\Phi}{\Delta H} t^2 \]

This represents volatile products during the endothermic decomposition of a spherical sample where \( K_0 \) is the linear constant and \( \Delta H \) is the heat of the reaction.

*Thermochim. Acta, 3 (1971) 1-12
B. Nucleation according to exponential law\textsuperscript{7,40}

\[ x = 1 - \exp(-Kt^p); \quad \frac{dx}{dt} = kx^n(1-x)^m \]  

(18)

where \( n \) lies between 1/2 and 1 and \( m \) between 0.774 and 0.556 corresponding to integer numbers of \( p = 2, 3, 4 \). For both \( m \) and \( n = 1/2 \), the rate of reaction was found to be proportional to the difference between interfaces of reacting solids\textsuperscript{36}. For further reaction progress see Eqns. (20) and (21).

c. Process is governed by nucleation followed by the bulk growth of nuclei

(Nucleation proceeds according to the exponential law, see Eqn. (18)).

A. Induction stage\textsuperscript{7,41,43}

\[ x = Kt^p; \quad \frac{dx}{dt} = kx^n \]  

(19)

where \( p \approx 4 \) and \( n \approx 3/4 \). This equation is also suitable for the description of the linear rate of nuclei growth when the rate of nucleation is negligible\textsuperscript{36}.

B. Two-dimensional growth of nuclei\textsuperscript{7-8,43} (Avrami equation)

\[ -\ln(1-x) = Kr^2; \quad \frac{dx}{dt} = k(1-x)(-\ln(1-x))^{1/2} \]  

(20)

C. Three-dimensional growth of nuclei\textsuperscript{7-8,43} (Avrami equation)

\[ -\ln(1-x) = Kr^3; \quad \frac{dx}{dt} = k(1-x)(-\ln(1-x))^{2/3} \]  

(21)

D. Later stages (unimolecular decay law)\textsuperscript{41}

\[ -\ln(1-x) = Kt; \quad \frac{dx}{dt} = k(1-x) \]  

(22)

or random nucleation with one nucleus on the individual particle\textsuperscript{17,32}. This form of the equation may also describe some cases of the decomposition and/or volatilization of pure condensed phase systems in which the reaction occurs homogeneously\textsuperscript{36} and without dilution of the reactant by reaction products.

[E. Interaction of nucleation frequency (for \( p > 4 \) increasing and for \( 3 \leq p \leq 4 \) decreasing) and time\textsuperscript{42}

\[ -\ln(1-x) = Kt^\nu; \quad \frac{dx}{dt} = k(1-x)(-\ln(1-x))^{p-1/\nu} \]  

(23)

where \( (p-1)/\nu \) is between 2/3 and 3/4. For \( p = 0.63 \) this equation may also be used to describe bimolecular reactions\textsuperscript{36}. Mathematically, this is the appropriate form of the differential expressing Eqns. (18) and (31).]
d. Process is controlled by nucleation followed by the linear growth of nuclei

A. Chain growth of nuclei including the possibility of their branching\textsuperscript{7,44}
\[ \frac{\alpha}{1 - \alpha} = K \exp(-K't); \quad \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\alpha \]  
(also explosive reactions where time has a large power, \[ \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\alpha^n \text{ for } n \gg 1 \text{\textsuperscript{44,53,54}} \])

B. Branching nuclei interacting during their growth\textsuperscript{7,45}
\[ \ln \frac{\alpha}{1 - \alpha} = Kt; \quad \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\alpha(1 - \alpha) \]  

C. Later stages of A and B\textsuperscript{7,45}
\[ \ln \frac{\alpha}{1 - \alpha} = K \log t; \quad \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\alpha^n(1 - \alpha)^m \]  
where \( n < 1 \text{ and } m > 1 \).

e. Diffusion-controlled reactions

A. One-dimensional transport process with constant diffusion coefficient (parabolic law)\textsuperscript{32-35}
\[ \alpha^2 = Kt; \quad \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\alpha^{-1} \]  

A similar equation, \( \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\alpha^{-n} \), may also be valid for some cases of sintering where \( 0 < n < 1 \), or possibly in the form of Eqns. (30) and (31)\textsuperscript{9}.

B. Two-dimensional transport process (\textit{e.g.} for a cylinder with no volume change during the reaction\textsuperscript{46})
\[ (1 - \alpha) \ln(1 - \alpha) = Kt; \quad \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(-\ln(1 - \alpha))^{-1} \]  

C. Three-dimensional transport process in a sphere* (Jander's equation\textsuperscript{32-34,47})
\[ (1 - (1 - \alpha)^{1/3})^2 = Kt; \quad \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k'(1 - \alpha)^{1/3}((1 - \alpha)^{-1/3} - 1)^{-1} \]  
\[ \approx k(1 - \alpha)^{1/3}(-\ln(1 - \alpha))^{-1} \]  

*These integral equations are difficult to simplify into a suitable differential form and thus an approximation is necessary:
\[ (1 - \alpha)^{-1/2} \approx 1 + (1/3)x + (4/18)x^2 + (21/162)x^3 + \ldots \]
\[ \ln(1 - \alpha) \approx -(x + (1/2)x^2 + (1/3)x^3 + (1/4)x^4 + \ldots) \]

The Ginstling and Brounshtein equation\textsuperscript{33,48,49}

\[ 1 - 2/3 \alpha - (1 - \alpha)^{2/3} = Kt; \quad \frac{dz}{dt} = k'((1 - \alpha)^{-1/3} - 1)^{-1} \]

\[ \approx k(-\ln(1 - \alpha))^{-1} \]  

(30)

[D. Growth of spherical particles during their precipitation determined by diffusion\textsuperscript{50} and expressed by an approximate form of the differential equation\textsuperscript{36}

\[-\ln(1 - \alpha) = Kt^p; \quad \frac{dz}{dt} = kz^p(1 - \alpha)^m \]

(31)

where \( p = 3/2, 2, 5/2, 3 \) depending on interface reaction and particle size and geometry\textsuperscript{50}. Some other authors give \( p \) a value below 0.5 in the diffusion region\textsuperscript{36}.]

**DISCUSSION**

A consideration of all cases of the mechanisms mentioned above with regard to the function \( f(\alpha) \) in the differential Eqn (2) seems to indicate that it is possible to express this function in a more analytical form (there has been no attempt to give a complete enumeration). The most convenient approximation can be considered to be as follows:

\[ \frac{dz}{dt} = k(1 - \alpha)^n z^m ( -\ln(1 - \alpha))^p \]  

(32)

thus rendering a proper combination of exponent-factors \( n, m \) and \( p \) and a mathematical description of the majority of possible mechanisms.

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If the relationship

\[ ((1 - \alpha)^{-1/3} - 1) = B_0(-\ln(1 - \alpha)) \]

is assumed, it is possible to establish the tendency of \( B_0 \). The value of \( B_0 \) was computed as a constant using 5 terms of the series written above by means of IBM/360 for \( x \) from 0.1 (step 0.1) to 0.9

\[ z \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \quad 0.9 \]

\[ B_0 \quad 0.339 \quad 0.346 \quad 0.354 \quad 0.363 \quad 0.373 \quad 0.384 \quad 0.396 \quad 0.409 \quad 0.423 \]

The maximum deviation from the average value for \( B \) is about ±10%. This is quite suitable having regard to the accuracy required for the experimental data and the activation energy. Thus the average value of \( B (\sim 0.376) \) may be included in the pre-exponential factor of \( k \), see Eqns. (29) and (30). The above series of \( B_0 \) may also be adopted in the actual evaluation.
Combination of

\[ n \quad m \quad p \]

is suitable for:

- **O O O** Phase boundary reaction (linear Eqn. (14))
- **× O O** Phase boundary reaction (Eqns. (15), (16))
- **O × O** Unimolecular decay law (Eqn. (22))
- **O O ×** Nucleation (Eqns. (17), (19)), linear growth of nuclei (Eqn. (24)), linear diffusion (Eqn. (27))
- **O × ×** Diffusion (Eqns. (28), (30))
- **× O ×** Nucleation (Eqns. (18), (25)), latter stages of linear growth of nuclei (Eqns. (25), (26)), diffusion (Eqn. (31))
- **× O ×** Growth of nuclei (Eqns. (20), (21), (23)), diffusion (Eqn. (30))
- **× × ×** Unjustified as yet
- **× × ×** Any complicated case, unjustified as yet

This equation appears to be suitable for the algorithmization of the preliminary estimation of the probable reaction mechanisms either when fitting experimental data \( dz/dr \) and \( \alpha \) into different combinations of two exponent factors of Eqn. (32) in order to get a constant value for \( k \), or by direct computation of the combination of two factors (e.g. by matrix evaluation). The suitability of such a treatment can be justified only by the evaluation of known experimental data. This discussion touches only upon theoretical points of view.

This procedure, however, cannot give the direct answer in the search for a true reaction mechanism. The overlapping of the values of the exponent-factors, as well as the expected difficulties with the numerical solution of Eqn. (32) will provide only a rough idea of a spectrum of possible reaction mechanisms. Therefore a complementary direct investigation of the process by means of X-ray diffraction and/or microscopy becomes necessary. This should be included in all kinetic investigations.

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The most debatable and discrepant viewpoints of non-isothermal kinetics are discussed in the form of twelve questions and answers. The reputation of non-isothermal kinetics when carried out by thermoanalysts; the consequences of simplified concepts transferred from the kinetics of homogeneous reactions; the physical meaning of basic kinetic parameters in solid-state processes; the kinetic compensative effect and interdependence of kinetic parameters using the Arrhenius rate constant; the mutual usefulness of differential and integral methods of kinetic data evaluation; their accuracy and correctness; the reliability of DTA measurements; non-isothermal versus isothermal investigations; equilibrium and kinetic data and their mutual effect; the extended discussion initiated by MacCallum and Tanner; non-isothermal data publication policy; and finally the use of computers.

Instead of an introduction

An article which would contain merely questions with their answers on some notoriously discussed but not yet clear topics of the fashionable kinetics of non-isothermal processes first came into my thoughts on the basis of the remarks presented at the panel discussion at the TA seminar on kinetics held in Budapest, in July 1972 (Berggren, Jesenak, Pungor, Zsakó). This idea, however, survived untouched until the meeting of Hungarian thermoanalysts in Balatonfüred in October 1976, where it matured during the round-table discussion (Dollimore, Meisel, Oswald, Rouquerol). The written form was finally encouraged by J. Simon, editor of JTA.

The problematics of description of non-isothermal processes fall into two categories. The part dealing with the more rigorous thermodynamic aspects and definitions of experimental conditions and thermophysical experiments in general was published in TCA 28/2 in 1978 in the form of a classical type of review. The present part intends to pay attention to some controversial viewpoints regarding non-isothermal kinetics, which sometimes intentionally and sometimes by mistake veil the consequences of dynamic experiments. This untraditional form for a review seeks, last but not least, for possibly better answers to those questions which are felt not to have been explained in a satisfactory manner, or which have
not been taken into account as yet. This also remains a task for the reader's own consideration when studying the article.

It should further be mentioned that this approach was affected by the discussions held during the German autumn school on kinetics, in Eisenach in 1977 (Anderson, Heide, Ludwig, Schultze). My thanks are also due to my friends and co-workers, particularly V. Satava and P. Holba, for a long, cheerful, as well as most creative cooperation, and for their frank discussions on all aspects (reasonable and even crazy) of philosophy and science.

Questions and answers

(1) **Q:** Why has non-isothermal kinetics gained such a bad reputation? Is it due to experiments carried out mainly by thermoanalysts?

**A:** Any advent of commercial apparatus production sophisticated stage of automatization and even pressing development of evaluating techniques makes it easier to produce nice curves and other digital or punched output ready for further mathematical treatment. As already long ago, this has tempted many investigators to determine easily attainable parameters of processes called kinetic data [1]. The result is well known: a number of scientific reports containing information with varying degrees of reliability. It is evident that those making classical investigations of kinetics have attacked non-isothermal studies. This has consequently resulted in a rather great disrespect for non-isothermal studies, and in some restrictions with respect to the publicability of such data in some of the more recognized journals.

Let us take an example. In the literature we can find recipes on how calculate basic kinetic parameters, regardless of their true physical meaning. What is more, this is often applied to a most complicated case, i.e. DTA measurements of solid-state processes. For instance we can draw by hand a curve in the form of a DTA peak and then calculate certain numerical data: the activation energy by Piloyan's method [2] and the reaction order by Kissinger's method [3]. There is certainly something out of order, as nobody can extract the similarly important thermodynamic data so easily without some additional specifications as to the curve origin (material and experiment). The puzzle of such a non-isothermal kinetic treatment is a fairly good coincidence with the analogous data established with complementary measurements. In spite of this we can easily see some lack of logistics or, at least, the insufficiency of the physico-chemical grothwork in some branches of non-isothermal kinetics. However, I by no means want to increase any consciousness of thermoanalytical society that all non-isothermal data ought to be treated with great caution, as was felt during the 5th ICTA in Kyoto. I am aware that any critique of the present kinetic procedures because of they unsatisfactory description of the reality of e.g. heterogeneous reactions is much easier than making a new proposal how to substitute it by more suitable theory. Therefore
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the rejection of the present mode of the calculation of certain parameters which we want (although not always may) compare is not a solution at all.

(2) Q: Non-isothermal kinetics, in fact, is liable to pay for the mode of its historical introductions. Where are the roots of possible misfits and where can we best learn the basis of non-isothermal treatments?

A: Probably the first description of a non-isothermal treatment of TG data was reported by Van Krevelen, Van Heerden and Hutjens in 1951 [4]. The real progress was started by the work of Murray and White, Tsuzuki and Nagasava (for detail see [1]) Kissinger [3] and Freeman and Carroll [5] in the late fifties. The first concise reviews came in the middle sixties [6–8]. However, we should not forget the pioneering work of Akahira [9] who introduced the integration of the temperature-dependent exponential in the late twenties.

Unfortunately, all the above articles carried along the basic terminology by analogy with the adopted kinetics appropriate for the description of homogeneous reactions in gases and/or liquids. However, this was an understandable result of an easy treatment of the concept of reaction-order to surmount the initial mathematical difficulties. Later on, the continuous schematic and sometimes blind transmission of such premises led to problems in the application of the non-isothermal treatments to heterogeneous processes. This has been the subject of severe criticism [1, 10], but many of these notorious oversimplifications survive. Nevertheless, I do hope never to read again introductory sentences such as “solid-state process may be represented by a simplified kinetic relation defined by reaction order…”

The present state still needs a monograph truly devoted to non-isothermal kinetics. The existing literature deals either with homogeneous reactions or with a formal description of heterogeneous processes* [1, 11]. Some reviews have been published in JTA [12, 13] as well as in the Proceedings of ICTA conferences [14].

Otherwise, much useful information is scattered throughout all these scientific journals which still dare to print articles on non-isothermal kinetics. The ratio of the contributions on the different kinds of kinetic analysis was searched for in two most representative TA journals (see Table 1). Although no steady trend towards a definite sort of kinetics has developed as yet, it is worth noting that the first signs of a new, actually non-isothermal approach are to be seen [15, 16].

(3) Q: What do kinetic parameters such as activation energy and reaction-order really mean? Are these terms generally applicable, particularly assuming solid-state processes?

A: From the textbooks we know well what these terms express, i.e. we can ascribe a definite meaning to the activation energy $E$, e.g. for the reaction of

* There also was published a book by E. Koch: “Non-isothermal Reaction analysis” which unfortunately I have not seen as Plenum Press refused to provide it for reviewing. A book by K. Heide about non-isothermal kinetics of heterogeneous processes is announced to be published in Berlin. Another book including kinetics of solid state reactions is in the course of preparation by author to be published jointly by Academia and Elsevier.
gaseous iodine with hydrogen either by coordinate energy calculation or by the
scholastic approach. It is, in fact, a potential barrier separating the initial and
final states. At the moment when we admit one reactant to be a solid phase, the
above reaction scheme presumably loses its validity; nevertheless it can still yield
certain numerical values. Consequently the rate constant is affected by the choice
of a kinetic model and may be found in the form of a power. Such an exponent is
a function of nuclei formation, interface and mass transport, and thus the analytical
formulation of the kinetic equation becomes a decisive step. The parameter
$E$ fitted to the given kinetic equation is understood as a derived constant and is
of limited validity. The obligatory expressing of $E$ in the dimension of energy
per mole is retained as a practical result of multiplication by the gas constant
(compare for example, phase-boundary processes). The overall (apparent) value
of $E$ is not always a primitive value for nucleation-controlled processes [17].
It is composed of partial energies associated with nuclei formation, crystal growth
and diffusion, and altogether may reach a rather large value. Experimentally,
such a process exhibits a very sharp, explosive-like course; its surprisingly high
barrier thus does not permit the process to occur thermally until the barrier is
finally surmounted the reaction then rocketing at full speed. On the other hand,
the reactions which are limited by mass transport show a rather low value of $E$,
although the diffusion seems to be a smooth process taking place within a compar-
atively large time-temperature interval. For metals it may be well interpreted
by a defect-walk mechanism [1, etc].

In contrast to the physico-chemical approach, we must admit that the reaction-
order concept may be an adequate tool for finding the most favourable conditions
to control and carry out an engineering process satisfactorily. It may be assumed
that not much care is directed to the reliability of the mathematical description
nor to the correctness of the kinetic parameters. The aim is merely a formal fit
of the experimental data using the simplest form of polynomials, to be able to
compare reaction rates or energy barriers for various experimental conditions in
a sensitive enough manner.

No less important is an appropriate choice of the experimental set-up and
measuring conditions to match the conditions of the process in question. It is
evident that the thermogravimetric investigation of micro-samples in vacuum is
of little applicability to the industrial process of the burning of limestone, while
the study of the decomposition of a ball-like sample at least 10 mm in diameter
may provide useful data as regards not only the chemical character of the process,
but more likely to its geometric aspects, mass and heat transfers, etc.

In addition one must keep in mind that a bad kinetic result either due to pure
and undefined sample and/or vague experimental conditions cannot be veiled by
any resonant nor ingenious mathematics. That is, “experiment does not have to
agree with our theory and process never obeys our equations” [10, 14b].

(4) Q: Some authors advocate either the separability or non-constancy of kinetic
data. Is this true, and how is it related to the so-called kinetic compensation effect?
A: Although this is connected with the preceding question, it is worth discussing
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separately. Let us first talk about the "Arrhenius" rate constant, \( k(T) \), itself, which has a general validity for thermally-activated processes, where either diffusion and/or phase-boundary chemical reaction are effective as basic rate-controlling processes. \( k(T) \) is then composed of the pre-exponential factor, \( A \), describing the frequency of attempts to surpass an energy barrier \( E \) of the process, and the exponential, \( \exp\left(-E/RT\right) \), expressing the probability of successful attempts. It was argued that the lack of an energy statistical distribution in real solids rules out the use of this concept [14b]. This certainly would deny the fifty years' work of famous scientists in the field of heterogeneous kinetics although a certain criticism of mechanically derived models upon oversimplified geometric systems is in its place. At least from a viewpoint of general relaxation processes we ought to admit that there always exist an (energetic) hinderance separating initial and final states which must be surmounted if the process is to advance even it is located to certain sites.

For a fixed value of the exponential, the constant ratio \( (E/T) \) must be maintained by the equal compensation of changes in both the numerator \( (E + \Delta E) \) and denominator \( (T + \Delta T) \). Similarly, for a fixed value of the reaction rate, the change of the whole exponential must be compensated by the change of the pre-exponential factor. For reasonable values of reaction rates, we thus cannot obtain the mutually independent values of the kinetic parameters \( (E \) and \( A) \). As a consequence for high-temperature processes (\( T > 1500 \) K) we find greater values of \( E (E > 100 \) kcal) and \( A (A > 10^{18} \) s\(^{-1}\) ), which certainly lend to difficulties in their theoretical interpretation [18]. The interdependence of kinetic parameters can be best demonstrated through the theoretical construction of artificial TA curves with respect to their position within the \( T \)-coordinates and the magnitude of the kinetic parameters [19], which is a frequent and often recurring subject of kinetic reports of (cf. [1]). Nevertheless, it reflects sensitively any case where the rules of our kinetic game are not fulfilled. It may happen when the temperature-dependence of \( A (= \lambda T^b) \) is not accounted for and/or the inappropriate model relation \( F(\alpha) \) (instead of \( f(\alpha) \)) is employed. In such a case the kinetic compensation effect can be understood as a misfit to be described analytically by equations: \( \bar{E} = E - b RT \ln T \) or \( \bar{E} = E - RT [\ln F(\alpha)/f(\alpha)] \). So far, it is still an open question how much the experimentally-found thermal dependence of \( E \) is an entirely physical property of it or merely a result of non-uniform experimental conditions and homogeneity of material or inadequate mathematical treatment. Adonyi [20], for example, emphasizes that the examination of the function: \( \log A \) versus \( E \), together with the motion of coordinate axes, when taking into account the measuring conditions, can only give deeper information about the kinetics.

(5) \( Q \): Which method of kinetic data evaluation is better, differential or integral? (quite a common question!).

\( A \): Every method has its positive merits, as well as disadvantages, associated with the mathematical treatment itself and further affected by the demand for experimental data of a certain quality and extent. The principal classification can be seen from the following scheme:

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The differential method of kinetic data evaluation can be understood as the basic method, as it utilizes the primitive form of kinetic equation, i.e., $\dot{\alpha} = k_T f(\alpha)$. It requires threefold input data sets, the reaction rate usually being the derived one. Generally, any derivation or differentiation exposes the resulting equation to its becoming more distinguishable with respect to the experimental input data, but also more time-consuming and sensitive as regards their fineness (namely $\dot{\alpha}$). A simple comparison of the results obtained by various formal forms of $f(\alpha)$ function based on an increasing number of reaction-order-like exponents may not provide any deeper information about the mechanisms involved, because the closeness of the relation between the calculated and measured data is increased to a limited extent [20].

By integrating this primitive kinetic equation, one obtains such a form of kinetic treatment where only twofold experimental data sets are needed. Such a method is then presumably less laborious as well as less sensitive to experimental errors (scatter in $\dot{\alpha}$ is avoided). This, of course, is on account of the model relation distinguishability, i.e. the analytical forms of model relations $g(\alpha)$ overlap each other for the different cases of rate-controlling processes, $f(\alpha)$ [21]. The foundation of these methods is complicated by establishing the so-called exponential-integral function $p(x)$ [9], which is obtained through the integration of the rate constant $k_T$ within the temperature limits.* The practical evaluation by integral methods is comparatively easy, but requires certain assumptions about the behaviour of the $p(x)$ function [1]. It often results in the double-logarithm plot, because the $g(\alpha)$ function usually exhibits the logarithmic form itself, particularly for nucleation-growth processes. It is worth quoting an article in the Journal of Irreproducible Results saying that multilogarithmization is the most recommended way of all to diminish sensitivity. Certainly, this is not directed at the condemnation of the utilization of integral methods, but should rather be understood as suggesting caution in searching for the true limits of the applicability of integral methods.

In this place the incorrect treatment based upon the derivation of Johnson–Mehl–Avrami–Kolgomorov–Yerofeev (nucleation-growth) equation is worth noting. It results from the origin of this equation as derived already by the integration at constant temperature. Introducing $p(x)$-function to this primary

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* It is worth noting that Reich [22] once accomplished such an integration by simply separating the exponential in front of the integral ($\sim \int dT = AT$), which was evidently subjected to severe criticism [6]. Nevertheless, recent articles showed that after long and complicated mathematical manipulations one reaches a similar result [1, 4, 6] indicating that nature always tends to simple solutions.

* * *  

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integration makes it correct and leads, fortunately, to the same result differing only by a constant [29].

In contradiction with the preceding methods, where a linear temperature increase is assumed, a priori, the double-derivative method (which has not been officially named as yet) permits introduction of the actual temperature increase, through $T$ and truly instantaneous values of $T$. This, of course, is manually too difficult and experimentally too sensitive for elaboration, and hence is not yet popular.

For successful kinetic evaluation we should always bear in mind the purpose of our kinetic analysis and the means we have at our disposal for its realization. Methods of kinetic data calculation should not be self-satisfying and nor should we be blind to their possible shortcomings.

(6) **Q:** What about the accuracy of kinetic data calculation? Is this only a consequence of the accuracy of the experimental input data, or can it be further affected by its mathematical treatment?

**A:** First of all we must distinguish not only the accuracy of the numerical values calculated, but also their correctness, i.e. the coincidence between our mathematical model (namely the $f(z)$ function) and the actual process under investigation (only the data fulfilling both conditions are reliable). The diligent improving of numerical accuracy is typical evidence of how much importance is laid on mathematics and how little on logistics, as can be found in numerous articles trying to settle the accuracy after the decimal point [1]. In the light of some poorly-defined experiments such refinements are ludicrous if one imagines the possible misfit introduced by a false application of unreliable kinetic models. On the other hand, we cannot deny the definite mathematical skill and wittiness of the theoretically-oriented articles, which, however, sometimes falls beyond the range of normal kinetics, e.g. the reports refining the calculation of the $p(x)$ function. Everyone can remember that once it was fashion to search for a new rearrangement in mathematical analysis and to be frank, many of us non-isothermal kineticists must admit to the dream of discovering a new method of kinetic treatment to be named after the author. However, in most cases this ended in the knowledge that the arithmetics did not leave much space for success. As side-effect, the accuracy of different kinetic evaluations was listed mainly for different kinds of integral methods established through different ways of exponent-integral expansion. Finally there appeared the still underestimated article by Broido and Williamson [21], who diagnosed exactly what integral method yields the most accurate result by distinguishing the accuracy of individual polynomials hidden in individual kinetic treatments. For instance there are the common plots of $\log g(z)$ vs. $\log T$, $AT$ vs. $1/T$, the last more accurate than the first one. Nevertheless, further new such reports have very recently been published showing the notorious desire to increase the ways of deriving methods of kinetic data evaluation and to improve the numbers of resulting kinetic constants, not considering that any deviation in $E$ under comparable conditions of the same $g(z)$ always gets within the limit of $\pm 10 \text{ rel}\%$ of $E$, well accepted in all kinetic studies. This is less impor-
tant than the reliability of the \( g(\alpha) \) function, the correct establishment of which should be the real goal of chemical kinetics.

(7) \( Q: \) There are controversial view regarding the reliability of the most popular TA method: DTA. Is it useful for kinetic studies or is it too dependent on its experimental set-up and thus more suitable for analytical applications only?

\( A: \) As already noted in the first question, the oversimplifications of kinetic analysis of DTA data led in many reports to the popular plot of \( \log \Delta T \) vs. \( 1/T \) [2] to extract \( E \) from the slope. It certainly provoked much criticism [10, 24, 25] directed to all unclear and questionable aspects of DTA, going sometimes so far as to condemn completely the use of DTA in kinetic studies. This is quite understandable if we imagine the complicated relation between the measured \( \Delta T \) and searched \( (\alpha) \) properties. In this DTA equation [26] particularly the term containing \( \Delta T \) is often neglected, although it expresses the important fact that the heat cannot be delivered to the sample infinitely quickly. When searching in the classical articles about DTA (Borchard and Daniels [27], we can already observe that the Piloyan plot [2] ought to be written as \( \log (C_p \Delta T + k_{\text{DTA}} \Delta T) \) vs. \( 1/T \), where \( C_p \) and \( k_{\text{DTA}} \) are heat capacity and DTA apparatus constant, respectively; this has been employed so far only twice [28, 29]. What is worth noting again, is the embarrassing coincidence between DTA kinetic data and those obtained under comparable conditions. Is there a real picture of a chemical process in the study, or does it report the constants of mass and/or heat transfer. All the same time, however, we must emphasize that such experimental data as those of DTA contain actual information about the non-stationarity of the system, and it is only up to the interpreter how to decipher the curves. This is not easy, as has been demonstrated in numerous articles utilizing gradient theory (Eriksson [30]), Laplace transforms (Takeo [31]), Green's functions (Akita [32]) and other high mathematics, that have not received the deserved attention. This is probably because the TA experimenter has not much time to get through high theory, and even with the aid of computers he tends to deal with easily understandable approaches like the model based on the phenomenological description of heat-exchange between two bodies of uniform temperatures [26].

DTA measurements are, in fact closely dependent on our experimental inability to maintain a strictly linear temperature increase. If we diminish the temperature deviation, the DTA peak also disappears. An increasing amount of generated heat yields a relatively higher temperature gradient and heat-exchange which may contribute to the DTA peak formation. In the first approach this may be neglected when the different heating rates affect the value of \( E \) by less than \( \pm 15\% \). The different sizes of DTA peaks also have no effect in the logarithmic representation if the peaks are geometrically similar. A small deviation of the true sample temperature \( (T) \) from the programmed linear increase \( (T=0 = \text{const}) \) may be negligible if the temperature interval of the peak is comparatively large. A good coincidence between DTA and optical microscopy data is shown in [29] on crystallization of glass.

(8) \( Q: \) If there are so many troubles with the gradients, would it be better to

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employ only isothermal methods? What, in fact, is the difference between iso- and non-iso-data?

A: One of the most important problems is the extraction of appropriate information from a given set of experimental data. Let us define an isothermal process as a progress of the state of the system at constant temperature as a function of time, where the measured property $Z$ is defined by the equations: $Z = Z(t)$, $T = \text{const.}$ For the system exposed to externally-applied constant heating, the non-isothermal process is defined by time-temperature sequences of its state, i.e., $Z = Z(t)$, $\dot{T} = \text{constant} = 0$. Such resulting data are, of course, more compact and may provide a wider but also a more complicated basis for their analysis.

Numerous authors argue that the system being heated is distorted by the creation of temperature gradients, i.e. $\dot{T} \neq \text{const}$. Fortunately, such a system reaches a quasi-stationary state ($\dot{T} + \Delta = \text{const}$) under steady conditions of heating. The constant distribution of gradients makes it possible to define the state of the system by an average value of the measured property, which is in accordance with the theory of phenomenological thermodynamics and which, moreover, agrees with the single-valued data provided mostly by all TA measurements. If a thermal process occurs, the steady state becomes dependent on the time-temperature progress of the process, and thus $\dot{T} \neq \text{const}$ and $T = T(t)$. In such a case, however, the isothermal course also becomes distorted, as the sample temperature is not constant either ($T \neq \text{const}$) due to self-cooling and/or self-heating of the sample. This fact is often neglected or forgotten, although it may have the same importance as in non-isothermal measurements. The advantage of non-isothermal experiments, however, is a continuous measurement of the instantaneous sample temperature, and its deviation from a predetermined course helps us to determine not only the progress of the temperature gradients but also the entire progress of the process itself, such as in the case of DTA (see the preceding question). For ordinary measurements we may be satisfied with certain mathematical simplifications which are adequate for the simple kind of TA instrumentation; but we always have to be aware of the limits and consequences of such simplifications. Any sort of treatment can thus be tolerated if the author recognizes its shortcomings and gives to it the necessary scientific aim. An intimate correlation of iso- and non-iso-methods may then lead to refining of the true meaning of the rate constant as well as the physico-chemical aspects of the process in question.

(9) Q: Can we ever speak about thermodynamics in terms of dynamic thermal experimentation, how compatible are kinetic and equilibrium data; and what then is the equilibrium background of the process?

A: Let us first put our system investigated by TA into the scale of classical thermodynamics (thermostatics) and rational thermodynamics as limiting cases. Assuming three basic quantities, $T, P, Z$, we may write for theoretically quasi-stationary TA process:

\[ J. \text{ Thermal Anal. 16, 1979 } \]
This, in fact, is in accordance with a well-known result following from the thermodynamics of an irreversible process, which says that for systems which are not too distant from their equilibrium state and in which the processes proceed quickly enough, the ordinary thermodynamic logistics and relations may be employed. Joint and concise mathematical descriptions of the dynamic (flux) and static (equilibrium) behaviours of such systems is not yet available and, anyhow, will be too complicated for normal use. Therefore, two separate disciplines have developed: thermodynamics, where we attempt to determine the equilibrium quantities by extrapolation to equilibrium conditions (\( \dot{T}, \dot{P}(\dot{Z}) \rightarrow 0 \)), and kinetics, where we try to describe the time-temperature development of the system equilibration (\( \dot{Z}, \Delta T, \Delta P \)). It is evident that for the system in equilibrium (\( dT, dP, (dZ<) \)) it is meaningless to speak about kinetics, as there is no driving force for any change (only time-temperature fluctuations). On the other hand, when the temperature of the system is continuously raised, the equilibrium conditions may also be gradually shifted, creating the so-called equilibrium background of the process. This is important for processes which proceed within a certain temperature interval (variant processes and/or diffuse first-order transformations), such as melting in a two-phase region [33]. This effect is often neglected during non-isothermal investigations, although it ought to be incorporated into the calculation in the form of the propagation of equilibrium under the idealized conditions of infinitely slow heating. High enough heating rates, however, enable us to evaluate the major part of a TA curve above the two-phase region, where ordinary kinetics is applicable again.

There is another influential factor: proximity to equilibrium, which should often be involved in our mathematical operations. Temperature integration of the rate constant yields, in fact, the difference of two \( p(x) \) functions \( [p(x) - p(x_0)] \), in which the second part may be neglected only when the measurement is carried out at temperatures distant from the equilibrium temperature. This becomes important for reversible processes studied at low heating rates, so that a great portion of material reacts in the vicinity of equilibrium [34]. Inclusion of the driving force (\( \Delta G \)) into the primitive form of the kinetic equation yields the rate constant in a more complex form: \( k_T(1 - k_G) \). Accordingly, the integration becomes more complicated, giving as many as four \( p(x) \) functions [13]. Hence,
it is evident that appropriate knowledge of the kind of process investigated, with an adequate choice of measuring conditions, particularly the heating rates [1], makes it possible to achieve reliable kinetic analysis.

Q: The year 1970 was full of activity in seeking the fundamentals of the correct representation of the non-isothermal kinetic equation, which was initiated by MacCallum and Tanner's article. What in fact is the essence of this problem? 

A: In principle this concerns the mathematical formulation of a basic kinetic equation valid under non-isothermal conditions. Two time-dependent variables ($t$ and $T$) were put together to represent the state of the system ($x$). Upon a normal mathematical procedure of partial differentiation, this assumption leads to the dependence: $\dot{x} = (\dot{x})_T + (\frac{\partial x}{\partial T})_T \dot{T}$, in which the term $(\dot{x})_T$ is assumed to describe the isothermal rate only. This puzzle was first raised by McCallum and Tanner [35].

The wide public reaction showed again the danger of mere mechanical application of the mathematical symbols involved [36]. Let us investigate the true physical meaning hidden in such a relation, imagining a heated container filled with water, about which we assert that the content of water ($x$) is dependent merely upon its instantaneous temperature ($T$) and the time ($t$) since its filling ($t = 0$), regardless of whether any water still remains in the container. It is evident that this logistic approach is wrong, as we do not describe effectively enough the actual dynamics of the boiling process in question, i.e. the volatility rate ($\dot{x}$) as a function of ready-to-react material ($x$) at a given temperature ($T$) (compare question (8)).

Nevertheless, such discussion may be very instructive and such kinds of articles should from time to time be accepted for printing. In this place the editorial policy should be noted. An example is the case of philosophically oriented reply notes [37–39] published in Nature and following the article by MacCallum and Tanner [35]. Although the problem has not been sufficiently clarified [37–39]. Nature stopped accepting additional remarks, leaving this subject to be further discussed in "local" journals [36, 40, 41], possibly regarding it as "thermoanalytical business" only. In many cases it did not touch the point as yet [41, 42].

The wide kinetic community, however, may also feel the lack of the final word [42]. On the other hand, I touched on the above problem during my 1975 lecture at the Institute of Chemical Physics in Jerevan. To my surprise I learned that this puzzle was completely evident to those people dealing with the kinetics of adiabatic gaseous reactions. Here I probably approached one of the most painful sides of kinetics and nowadays possibly all scientific work in general: the lack of an appropriate exchange of information.

Q: Is it worth paying such attention to non-isothermal kinetics? Is it merely good for a narrow region of interested scientists, and how about the already-mentioned publication policy?

A: Well, it should be stressed once more that the problem associated with dynamic kinetic measurements has its significance in all branches of experimental kinetics, because truly constant experimental conditions are hard to achieve. Non-isothermal kinetics, as is obvious from recent articles printed in JTA and TCA, is primarily limited by the TA experimental technique, but is carried out
Table 1
Survey of the number (and rel. %) of kinetic articles* so far published in J. Thermal Anal. and Thermochim. Acta

<table>
<thead>
<tr>
<th>Year and journals</th>
<th>Number of reviewed articles</th>
<th>The part dealing with kinetics</th>
<th>Theory of formal approach</th>
<th>Application of formal approach</th>
<th>Formal mechanism (stoichiometry)</th>
<th>Theory of mechanism and kinetics</th>
<th>Mechanism and kinetic applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970 JTA</td>
<td>44</td>
<td>12 (27%)</td>
<td>4 (33%)</td>
<td>3 (25%)</td>
<td>3 (25%)</td>
<td>1 (8%)</td>
<td>1 (8%)</td>
</tr>
<tr>
<td>1970 TCA</td>
<td>77</td>
<td>12/21</td>
<td>1/8</td>
<td>5/41</td>
<td>5/41</td>
<td>1/8</td>
<td>2/17</td>
</tr>
<tr>
<td>1971</td>
<td>43</td>
<td>3/7</td>
<td>1/33</td>
<td>0</td>
<td>1/33</td>
<td>0</td>
<td>1/33</td>
</tr>
<tr>
<td>1972 TCA</td>
<td>74</td>
<td>17/23</td>
<td>5/29</td>
<td>2/12</td>
<td>5/29</td>
<td>3/18</td>
<td>2/12</td>
</tr>
<tr>
<td>1973</td>
<td>39</td>
<td>10/26</td>
<td>5/50</td>
<td>2/20</td>
<td>2/20</td>
<td>0</td>
<td>1/10</td>
</tr>
<tr>
<td>1975</td>
<td>68</td>
<td>15/22</td>
<td>3/20</td>
<td>6/40</td>
<td>4/27</td>
<td>1/7</td>
<td>1/7</td>
</tr>
<tr>
<td>1976</td>
<td>101</td>
<td>8/8</td>
<td>2/25</td>
<td>2/25</td>
<td>1/20</td>
<td>3/30</td>
<td>0</td>
</tr>
<tr>
<td>1977</td>
<td>120</td>
<td>24/20</td>
<td>6/25</td>
<td>10/42</td>
<td>2/8</td>
<td>4/17</td>
<td>2/8</td>
</tr>
<tr>
<td>1978 TCA</td>
<td>144</td>
<td>35/24</td>
<td>20/37</td>
<td>2/6</td>
<td>2/6</td>
<td>5/14</td>
<td>6/17</td>
</tr>
<tr>
<td>1977</td>
<td>91</td>
<td>34/37</td>
<td>9/26</td>
<td>15/44</td>
<td>7/21</td>
<td>1/3</td>
<td>2/6</td>
</tr>
<tr>
<td>1978</td>
<td>121</td>
<td>21/17</td>
<td>3/14</td>
<td>5/24</td>
<td>7/33</td>
<td>1/5</td>
<td>5/24</td>
</tr>
<tr>
<td>1979</td>
<td>77</td>
<td>26/34</td>
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<td>4/15</td>
<td>8/31</td>
<td>3/12</td>
<td>6/23</td>
</tr>
<tr>
<td>1979</td>
<td>148</td>
<td>26/18</td>
<td>2/8</td>
<td>7/27</td>
<td>5/19</td>
<td>5/19</td>
<td>7/27</td>
</tr>
<tr>
<td>1979</td>
<td>67</td>
<td>19/28</td>
<td>5/26</td>
<td>3/16</td>
<td>2/11</td>
<td>2/11</td>
<td>7/37</td>
</tr>
<tr>
<td>1979</td>
<td>237</td>
<td>49/21</td>
<td>12/25</td>
<td>15/31</td>
<td>8/16</td>
<td>5/10</td>
<td>14/29</td>
</tr>
<tr>
<td>Total</td>
<td>521</td>
<td>166/32</td>
<td>46/28</td>
<td>48/30</td>
<td>31/19</td>
<td>14/9</td>
<td>27/16</td>
</tr>
<tr>
<td>TCA</td>
<td>1066</td>
<td>201/19</td>
<td>53/26</td>
<td>46/23</td>
<td>39/19</td>
<td>30/15</td>
<td>40/20</td>
</tr>
</tbody>
</table>

* It presents a certain (subjective) view in ranking articles as those dealing with formal determination of kinetic data (reaction order) and its formal applications, analysis of reaction stoichiometry (mechanism), theory of reaction mechanism (kinetic models) and finally the applications of kinetic models in physical-chemical studies. (The number of articles compiled must not be identical with their actual number published in the year because of some missing issues.)

by numerous workers in different fields (cf. Table 1) (question (1)). The surprisingly low citation index is probably rooted in our preoccupation which often leaves insufficient time for a patient understanding of other authors work, logistics and particularly symbolics. A good example is the series of very narrow specialized
articles on the $p(x)$ function, following each other at an interval of about one year, but making little reference to the previous ones [42–49] although printed in similar journals (TCA or JTA). This, of course, is also subject to the quality of the referee's work, the importance of which is sometimes underestimated, particularly when considering the still explosive trend of kinetic publications.

Our often very sectorized specialization leads, unfortunately, to a certain type of ignorance concerning the other works on a similar theme. This results in easy self-citing, because our own past work is most simple to be understood again "usually with the little effort of one re-reading". I once read that the usefulness of our citations may be evaluated by a quotient obtained by subtracting twice the self-citations from the remainder, which should at least be positive. (Ref. 26 is not the best example.)

Another side is the efficiency of the written text. The repetition of previous results and/or theories, so obvious in kinetics articles, is sometimes powerless and so subject to severe criticism, but, on the other hand, it may help the reader to catch the point very quickly. The basic fault of most introductory lines is their dispersity and/or length. It might be a good idea to introduce a key (or code) system (similar to those employed for abstracting), making it possible to write an introduction in a standard, concise but summarized way, even avoiding redundant derivations.

Finally, I should also present a diffident comment regarding the elegance and legibility of scientific language, as recently emphasized in a very nice manner by Keatch [50]. Such discussion belongs certainly to those who possess English as their native language. Besides, the quality and amount of our work the beauty of a well-written scientific report should be a (goal and entire pleasure) of our activity, similarly to an artistic work.*

(12) Q: The offensive of computing techniques in all branches of science and engineering has not certainly avoided the field of TA. Will computers be of real help in our kinetic work, or will they solve only the most painful numerical troubles?

A: This question must be answered in a broader sense, as we must surely admit that in the near future all TA laboratories will be fully or partly equipped with computing equipment (hardware, software, microcomputers, etc.). The question hence should read: are we ready to accommodate the new methods of treatment in our everyday practice? Sophisticated sets have already appeared on the market, but their furnishing with standard programs (good for the late sixties, compare kinetic articles in TCA 1977) has brought again the danger of employing good mathematics in a rather poor physical sense. On the other hand, some terms from the computer language (slang) have become so fashionable in accelerating sales, that their real information content may be discredited.

The most important fact in data treatment is how the output signal from a TA apparatus is maintained. A typical chart record will probably persist so as to give

* I would like to support the proposal as to create an annual prize for the best presented paper appearing in either of TA journals and or ICTA proceedings.
an immediate, first-sight feeling as to whether the curve is of good or poor quality; however, the further elaboration of the curve then requires an enormous effort: an intermediate step of usually manual and time-consuming trace reading and numerical data preparation. Another problem arises for the preparation of short algorithms and for often changing mathematical procedures, where debugging, data punching and mechanical transfers are sometimes too slow and immobile in computing centers. The desk or pocket calculators provide a more direct and flexible service, and should become a new "logarithmic ruler" in everyday thermo-analytic work. Nevertheless, the most serious obstacle rooted in extensive numerical and statistical data treatment has been overcome. Of course, there may appear certain inequalities, hidden in the possibility of describing the system by sets of more sophisticated equations but where we may lack a sufficient amount of physical information relating to a single point measured ($T - x$ versus the sets of $\sum_i T_i - \sum_i x_i$ data). At the same time, we may not be ready to know how to interpret properly a new sort of output data which may not be in the form of single-valued constants or numericals.

More work should be done in using methods of chemical and mathematical statistics, information content and capability including its theory, hypothesis testing and goodness of fit tests, etc [51-53]. It would be recommendable to all author to get acquainted with at least some books on statistics [54] prior writing an article on numerical results.

A big qualitative step is the direct digitalization of the TA apparatus signal, which will presumably become a basic requirement for all TA experimentation. Entire on-line computing systems and possible self-control of TA experiments seems to be not too effective, because it may keep the computer busy with inadequate and rather mechanical work, such as temperature control, which is more suitable for cheaper microprocessors. We should not forget the analogous computers suitable for direct comparison of the experimental curve with the master curve or for solving differential equations, both of use in theoretical kinetics, whereas a digital computer must transfer this problem to the solution by matrices.

Looking back to the literature, probably the first computer polynomial fit was applied to a thermocouple signal [55]. It was followed by different tabulations, efforts either to make precise or list different functions, e.g. the $p(x)$ function. The pioneering work in non-isothermal kinetics was probably that by Anderson [56], who solved three simultaneous equations for different heating rates. Main activity, however, was focused on the evaluation of reaction orders and activation energies by using different simplified models [57, 58]. Only the most recent years finally brought up the problem of selection of appropriate mechanisms by fitting different analytical forms of $f(x)$ and $g(x)$ functions. This included correlation coefficients between the experimentally-determined and theoretical master curves as well as built in subroutines to evaluate the $p(x)$ function. No heavy-capacity algorithm, however, could give a direct and unambiguous answer to the basic kinetic question what the true reaction kinetics and mechanism involved. They
merely classified the output data to a list of more or less probable kinetic models for a given sort and quality of experimental data. Complementary information, additional analysis of their physical meaning or more sophisticated criteria are needed.

In conclusion, more space should be given to computing treatments in existing TA books such as [1, 60, 53]. Seminars should bring together specialists from computers and TA to teach other the ways and means of analogies and digital data elaboration and the process control in thermophysical experiments, the numerical treatment (derivation, integration, etc.), fitting and smoothing of experimental curves and the actual aim of analysis of TA data in order to face our new tasks. The first attempt was made by the Czech group on thermal analysis in Prague, at the meeting directed to the digital treatment and conversion of the TA output signal, numerical evaluation and information property of experimental data, and the theoretical basis of TA with regard to general problems of the extraction of physico-chemical quantities when using computers [59].

In concluding I would like to re-employ the generally oriented words that V. Šatava used in his introductory lecture on theory and experiment [59]. If we ask a laic what is the progress in natural science he would probably answer that it consists in the gradual growth of results of observations and experiments. But who is actually dealing with research knows that a mere data collection is of little value, and what more, would not be self-satisfactory because of the lack of excitement. The real aim of science is different; it seeks the knowledge about the rules which control the nature i.e. the understanding and consequent description of observed phenomena. The logistics and mathematics of facts with respect to their ordering is thus the most important procedure [61–64]. Complicated mathematics, however, is not alway the only way how to reach the answers. Philosophically oriented thoughts are sometime equally important if we can afford them in the present busy world. So that I personally much appreciate such aspects in our field of science: non-isothermal kinetics, as we can trace in the work of e.g. Boldyrev, Flynn, Garn, Ozawa Šatava or Segal etc. We also may remember not often cited words of some famous scientists as “when I ever had some success in mathematical physics it was because I was able to avoid mathematical difficulties” (Gibbs) and/or “do not disturb such a nice thing like science by mathematics” (Fermi). But would it be ever said in our age of computers?

References


J. Thermal Anal. 16, 1979

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RéSUMÉ — Les aspects les plus discutables de la cinétique non-isotherme sont traités sous forme de douze questions et réponses, en particulier: réputation de la cinétique non-isotherme appliquée par les thermoanalystes, conséquences des concepts simplifiés déduits de la cinétique des réactions en phase homogène, signification physique des paramètres cinétiques fondamentaux dans les processus en phase solide, effet de compensation cinétique et interdépendance des paramètres cinétiques lors de l'utilisation de la constante de vitesse d'Arrhenius, utilité mutuelle des méthodes différentielles et intégrales d'évaluation des données cinétiques, leur exactitude et leur degré de justesse, fiabilité des mesures par ATD, études non-isothermes vis-à-vis des méthodes isothermes, données à l'équilibre et en régime dynamique et leurs effets mutuels, extension de la discussion engagée par MacCallum et Tanner, politique de publication des données non-isothermes et finalement utilisation des ordinateurs et aide apportée par ceux-ci.


Резюме — В форме двенадцати вопросов и ответов обсуждены наиболее спорные и противоречивые точки зрения неизотермической кинетики. В частности рассматриваются известность неизотермической кинетики, когда она проводится термоаналитиками, послед....
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стия концепций упрощения, переносимых из кинетики гомогенных реакций, физический смысл основных кинетических параметров в процессах, протекающих в твердых телах, кинетический компенсационный эффект и взаимосвязь кинетических параметров при использовании константы скорости Аррениуса, взаимная полезность дифференциальных и интегральных методов выделения кинетических данных, их точность и корректность, надежность ДТА измерений, неизотермические исследования в сравнении с изотермическими, равновесие и кинетические данные и их взаимное влияние, расширенная дискуссия, начатая МакКэллом и Теннером, публикация неизотермических данных и, конечно, помощь и использование компьютеров.

J. Thermal Anal. 16, 1979
INTRODUCTION TO CHEMICAL KINETICS

Chemical kinetics is based on the experimentally verified assumption that the rate of change, \( \frac{dx}{dt} \), in the state of a system (characterized by) \( x \) is a function, \( f \), of the state alone, i.e., \( \frac{dx}{dt} = x' = f(x) \). Using this traditional postulation, the appropriate constitutional approach to inaugurate the desired constitutive equation can be written in the principal form of the dependence of the reaction rate, expressed as the time development of the normalized degree(s) of transformation, \( \alpha = \frac{(x - x_o)}{(x_o - x_\infty)} \), on the quantities that characterize the instantaneous state of the reacting system.

The reaction change is traditionally depicted in the form of a generalized equations, \( \alpha' = f(\alpha, T) = k(T)f(\alpha) \). Very important is to see the properties of the function, \( f(\alpha) \), which is liable for an appropriate match of temperature progression of reaction mechanism under study. The long-lasting practice accredited such a routine in which the function \( f(\alpha, T) \) is divided into the two mutually independent functions \( k(T) \) and \( f(\alpha) \) when traditionally assuming that \( f(\alpha, T) = 1 \). This implies that the rate of change, \( \alpha' \), is assumed to be proportional to the product of two separate functions, i.e., the rate constant \( k(T) \), dependent solely on the temperature, and the mathematical portrayal of the reaction mechanism, \( f(\alpha) \), reliant on the variation of the degree of conversion, only.

In chemical kinetics, the operation of \( k(T) \) function is customarily replaced with the known and well-defined analytical form of the Arrhenius exponential function, \( k(T) = A \exp(-E/RT) \), thoughtfully derived from the statistics of evaporation. The inherent constants are the so-called activation energy, \( E \), identified as the energy barrier (or threshold) that must be surmounted to enable the occurrence of the bond redistribution steps required to convert reactants to products. The pre-exponential term, or frequency factor, \( A \), provides a measure of the frequency of occurrence of the reaction situation, usually envisaged as incorporating the vibrating frequency in the reaction coordinate. The time-honored problem, however, is the mutual interdependence of \( E \) and \( A \), which arises from the mathematical consequences of the Arrhenius equation and which causes its use complicated.

There are also alternative depictions related to the activated complex theory and the partition functions of the activated complexes to give limited freedom along the reaction coordinate. The validity of the Arrhenius equation is so comprehensively accepted that its application in homogeneous kinetics normally requires no justification. Although the Arrhenius equation has been widely and successfully applied to innumerable solid-state reactions, this use factually lacks a theoretical justification because the energy distribution, particularly amongst the immobilized constituents of crystalline reactants, may not be adequately represented by the Maxwell–Boltzmann equation. Due allowance should be made for the number of precursor species within the reaction zone as well as for the changing area of the reaction interface. It can affect the enhancement of reactivity at the active sites (reaction contacts), exaggerated by strain (between the differently juxtaposed networks), defects, catalytic activity of newborn sites, irreversible re-crystallization, or perhaps even by local volatilization (if not accounting for the thickness of reacting zone contoured by local heat and mass fluxes across and along the interfaces). It brings multiple questions about its applicability and we can humorously cite: “Everybody believes in the exponential law of energy
distribution, the experimenters because they think it can be proved mathematically, and the mathematicians because they believe it has been established by observations”.

Nevertheless, it was shown that energy distribution functions of a similar form arise amongst the most energetic quanta. For values significantly above the Fermi level, both electronic energy (Fermi–Dirac statistics) and phonon energy (Bose–Einstein statistics) distribution approximate to the same form as that in the Maxwell–Boltzmann distribution. Also the interface levels, capable of accommodating electrons, are present within the zone of imperfections where chemical changes occur. These are analogous to impurity levels in semiconductors, imperfections levels in crystals (F-centers) and, similarly, can be located within the forbidden range between the energy bands of the crystal. Such levels represent the precursor energy states to the bond redistribution step and account for the increased activity relative to similar components in more perfect crystalline regions. Occupancy of these levels arises from activation through an energy distribution function similar in form to that characteristic of the Maxwell-Boltzmann equation and thereby explains the observed fit of \( k(T) \) data to an Arrhenius-type equation.

However, for the resolution of the second function, \( f(\alpha) \), we must act in a different way than above because the exact form of this function is not a priori known and we have to determine its analytical form (taking, in the same time, its diagnostic potential into our account). The specification of \( f(\alpha) \) is thus required by means of the substitution of a definite analytical function derived on basis of modeling the reaction pathway usually by employing some physical-geometric suppositions. In contrast to the determination of predefined characteristic parameters of the \( k(T) \)–function, the true purpose of kinetic studies is to hit upon this pathway, i.e., to find our imaginative insight into the reaction mechanism. Thus it is convenient to postulate a thought model visualizing the reaction, usually splitting it into a sequence of possible steps and then trying to identify the slowest step, which is considered to be the rate-determining one. Such models usually incorporate (often rather hypothetical) description of consequent and/or concurrent processes of interfacial chemical reactions and diffusion transport of reactants, which governs the formation of new phase (nucleation) and its consequent (crystal) growth. Such a modeling is often structured within the perception of simplified geometrical bodies, which are responsible to depict the incorporated particles and such visualization exemplifies the reaction interfaces by disjointing lines. Such a derived function \( f(\alpha) \) then depends on all such physical, chemical and geometrical relations, which are focused to the interface between the product and the initial reactant.

When not accounting on the interfaces or other in homogeneity phenomena we deal with homogeneous reactions determined by an averaged concentration in a whole reacting volume and thus the \( f(\alpha) \) function is paying attention to a most simplified description only, which is associated with the so-called reaction order. However, for solid-state reactions the reactants are neither mixed on an atomic level not equally distributed in the whole reactant volume and they must, therefore, penetrate, flow or diffuse into each other if the reaction is to start and propagate within the given volume. Accordingly the space co-ordinates become a controlling element, which creates heterogeneity effects inevitably to be included and which are actually accounted for creating interfaces by means of ‘defects’ conveniently symbolizing a pictographic contour (borderline, curve).

The mathematical description turns out to be much more complicated due to the fact that no mean ‘bulk concentration’ but the spot ‘phase interfaces’ carry out the most significant information undertaking the true controlling role for the reaction progress. The most common models are derived isothermally and are associated with the shrinking core of a globular particle, which maintains a sharp reaction boundary. Using a simple geometrical representation, the reacting system can be classified as a set of spheres where each reaction interface is represented by curve. We assume that the initial reactants’ aggregation must be reached by (assuming) well distributed (reacting) components (often through diffusion). Any such an interfacial (separating) layer, \( y \), bears thus the role of kinetic impedance and the slower of the two principal processes, diffusion and interface chemical reaction become the rate controlling process within the limits of our simplified modeling.
MODELING APPLIED IN CHEMICAL KINETICS

1) **Traditional kinetics:** the Arrhenius exponential parameter \( k(T) \) is introduced and the \( f(\alpha) \) function is modeled on basis of simplified physical-geometrical assumptions (growth/change of reaction interface).

2) **Phenomenological kinetics:** the Arrhenius exponential parameter \( k(T) \) is maintained but the \( f(\alpha) \) function is replaced by a suitable fitting (polynomials) or by fractal-like equations.

3) **Novel non-parametric kinetics:** mutually independent functions \( k(T) \) and \( f(\alpha) \) assume arbitrary function, i.e., both the Arrhenius parameter and model function are not connected with a specific reaction mechanism showing accidental-like relationship.

Let us first see the means of traditional kinetics schematically shown on the following figure:
Certainly, it brings a lot of simplifications regarding the true and idealized models, see bottom picture, but it provides a convenient list of models ready for application, which analytical forms are the traditional and repeated subject of most kinetic papers.

<table>
<thead>
<tr>
<th>Model:</th>
<th>Symbol:</th>
<th>Function $f(\alpha)$:</th>
<th>Integral form $g(\alpha) = \int_0^\alpha f(\alpha) d\alpha$:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation–growth</td>
<td>$A_m$</td>
<td>$(1-\alpha)[-\ln(1-\alpha)]^{1/m}$</td>
<td>$[-\ln(1-\alpha)]^{1/m}$</td>
</tr>
<tr>
<td>(JMAYK eq.)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase boundary</td>
<td>$R_n$</td>
<td>$n(1-\alpha)^{1/n}$</td>
<td>$[1-(1-\alpha)^{1/n}]$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>n-Dim.:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(equivalent to the concept of reaction-order $n$)</td>
</tr>
<tr>
<td>Diffusion controlled</td>
<td>$D_1$</td>
<td>$1/2\alpha$</td>
<td>$\alpha^2$</td>
</tr>
<tr>
<td>1-dim. diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-dim. diffusion</td>
<td>$D_2$</td>
<td>$-\frac{1}{ln(1-\alpha)}\alpha+(1-\alpha)\ln(1-\alpha)$</td>
<td></td>
</tr>
<tr>
<td>3-dim. diffusion</td>
<td>$D_3$</td>
<td>$(3/2)(1-\alpha)^{2/3}/[(1-\alpha)^{1/3}-1]$</td>
<td>$[1-(1-\alpha)^{1/3}]$</td>
</tr>
<tr>
<td>(Jander)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-dim. diffusion</td>
<td>$D_4$</td>
<td>$(3/2)[(1-\alpha)^{-1/3}-1]$</td>
<td>$1-2\alpha/3-(1-\alpha)^{2/3}$</td>
</tr>
<tr>
<td>(Ginstling-Brounshtein)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-dim. counter dif.</td>
<td></td>
<td>$(3/2)(1+\alpha)^{-2/3}/[(1+\alpha)^{1/3}+1]$</td>
<td>$[(1+\alpha)^{1/3}-1]^2$</td>
</tr>
<tr>
<td>(Komatsu-Uemura, sometimes called ‘anti-Jander’ equation)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Normal grain–growth</td>
<td>$G_n$</td>
<td>$(1-\alpha)^{n+1}/(n;r_o^n)$</td>
<td>$[r_o/(1-\alpha)]^n-r_o^n$</td>
</tr>
<tr>
<td>(Atkinson – long-range diffusion where $r_o$ is initial grain radius)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unsspecified – fractal approach (extended autocatalytic)</td>
<td>SB</td>
<td>$(1-\alpha)^n\alpha^n$</td>
<td>no particular</td>
</tr>
<tr>
<td>fractal-dimension</td>
<td></td>
<td></td>
<td>analytical form</td>
</tr>
<tr>
<td>(Šesták-Berggren)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is worth repetition that the above listed mathematical modeling can be broken into three major but reduced designs according to the downgraded reaction geometry. We can envisage either elementary process
(a) diffusion of reactants to and/or from the reaction interface through a continuous product layer,
(b) product nuclei formation and their consequent growth and
(c) chemical reaction restricted to the phase boundary.

These events can roughly concur to what can specifically happen when we try to measure and study the overall reaction path. There are no assured means that suchlike aggregated form of reactants would conduct themselves within our simplified picture and that the selection of a particular model is acceptable; however, a nuclei growth analysis shows as a rather useful tool for a preliminary screening of reactions within powdered compacts.

However, the modern mathematical tools of thermal physics make available powerful theoretical models employing nonparametric evaluations or neural networks to be associated with the true reality of natural processes that are never at equilibrium neither without gradients by appreciating the decisive role of thermal fluxes. In the scientific intent (often directed to generate publications based on non-isothermal kinetics), this approach has not yet been applied, but in the more urgent technological processing, such as industrially significant cement firing, ingot casting, arc melting or welding, which adoption became a real necessity to overcome manufacturing
difficulties. In particular, we can generally assume that at some distance from the reaction zone where the phase transformation (solidification) is taking place, the viscous (often molten) material undergoes irregular (turbulent) motion. It creates a mushy zone consisting of cascade of branches and side branches of crystals and interspatial melts, that remains lying between the original reactant (fluid) and the product (fully solidified region). Some chemical admixtures (as the alloy solution) are concentrated in the interspatial regions and ultimately segregated in the resulting micro-texture pattern. Such a highly irregular microstructure of the final solid can become responsible for alternative properties, e.g., reduced mechanical strength that is a costly factor thus worthy of active search as to resolve the intricacy of the processes involved. It follows that small changes in the surface tension, microscopic temperature fluctuations or non-steady diffusion may determine whether the growing solid looks like a snowflake, seaweed or spongy sinters. The subtle ways in which tiny perturbations at the reacting interface are amplified then become important research topics bringing necessarily into play either higher mathematics or non-Euclidean geometry of fractals.

The classical diffusion laws derived by Fick dominated physicist’s view on transport for more than a century. The recent observations, however, demonstrated its clear exemptions, which anomalosity were termed as “strange or fractal kinetics”, usually solved on basis on random walk approaches and unconventional distribution functions. Such a need for so called “fractional diffusion-advection equations” helps to a better understanding and prediction of the long-termed impacts of pollution on sizeable ecosystems and, for contrarily micro-systems, concerning the problem of a particle escape over a rigorous potential barrier.

For the continuous–time random walk (CTRW) the strict time interval between consecutive steps become governed by a waiting-time distribution, which stem from possible obstacles and traps that delay the particle’s permanent jumps and thus introduce memory effects into the transport motion. If the mean time diverges, as is the case for the common power-law waiting-time distribution, the mean squares displacement \(<x^2(t)>\) grows proportional to \(t^α\) with non-integral time power (\(n≠1\)). A consistent generalization of the standard diffusion continuity equation could still remain to be the second order in the spatial coordinates but is violated by exhibiting a fractional-order temporal derivative, such as \((\partial c(r,t)/\partial t) = k_n \nabla^2 c(r,t)\), where \(c(r,t)\) is the concentration of particles at some point \(r\) and time \(t\) (also corresponding the probability \(P(r,t)\) of finding a particle there). The diffusion coefficient \(k_n\) holds the dimension of \(L^2/T^n\) but may be replaced for the fractional diffusion by the coefficient \(L^2/T^α\) and such a fractional modification generate the scaling behavior often seen in inter- and sub-diffusion systems, which follow a complex relation \((\partial^α c(r,t)) = D^1/\nabla^2 c(r,t)\). It can be derived from CTEW scheme along the lines used in the Einstein’s work on Brownian motion linking normal diffusion with anomalous diffusion. A new mathematical description is thus introduced, which is called “fractional calculus” often applied to the derivative \(d^n y/dx^n\) when \(n\) holds an unfamiliarly non-integral value. Fractional derivatives proceeds from the repeated differentiation of its power, i.e., \(d^n y/dx^n(x^α) \approx \Gamma x^{α-n}\) (where \(\Gamma\) is the Gamma function) or by a more elegant way based on the fact that the \(n-th\) derivative is an operation inverse to an \(n-fold\) repeated integration providing the symbolic formulae of a general fractional derivative of the function \(f(x)\), i.e. \(D_{x}^{1-n}f(x)\).

It is clear that the reaction kinetics of solid-state processes involving time-dependent diffusion and nucleation did not absorbed as yet all possible means of modern mathematics to tackle the complex properties necessary to properly describe the reaction mechanism involved. It is assumingly due to its very demanding calculus, which is not simply compatible with “easy-drawn” geometrical models based on regular special portrayal of aggregated particles of someway regular shapes. It is recently supplied by the introduction of so called model-free descriptions, which use arbitrary mathematical function regardless their associations to model processes or point out their detailed mechanism, which is often in the crucial interest of the analysis of the process in question.

It was found useful to introduce a kind of pervasive description by means of a simple empirical function, \(h(α)\), containing the smallest possible number of constant. It provides some flexibility, sufficient to match mathematically the real course of a process as closely as possible. In
such case, the kinetic model of a heterogeneous reaction is assumed as a distorted case of a simpler (ideal) instance of homogeneous kinetic prototype \( f(\alpha) = (1-\alpha)^n \). It is mathematically treated by the introduction of a multiplying function \( g(\alpha) \), i.e., \( h(\alpha) = f(\alpha) \ g(\alpha) \), for which we coined the term ‘accommodation function’ and which is accountable for a certain ‘defect state’ (imperfection, non-ideality, error in the same sense as is treated the role of interface during the new phase formation).

It follows that the so-called empirical kinetic model function can be generally described by all-purpose, three-exponent relation: \( h(\alpha) = \alpha^n \ (1 - \alpha)^p \ [-\ln (1 - \alpha)]^n \). It is practically applicable as either form, Sestak–Berggren (SB) equation, \( \alpha^n(1 - \alpha)^p \), or modified Johnson–Mehl–Avrami–Yerofeev–Kolmogorov (JMAYK) equation, \( (1 - \alpha)^n \ [-\ln (1 - \alpha)]^p \).

Only the single exponents, such as, \( m \) (classical reaction order) or, \( p \) (traditional JMAYK equation with \( n=1 \)) or the two appropriately paired exponents are suitable for meaningful evaluation such as the classical model of self-catalyzes \( (m=1 \text{ and } n=1) \), which is thus a special case of the general SB equation. The justified and proper complementary couples are only \( (m+n) \) or \( (m+p) \), whilst the pair \( (n+p) \) exhibits an inconsistent role of two alike-functions, which are in an inadmissible (self-supporting) state.

The SB-equation \( \alpha^n(1 - \alpha)^p \) subsists the generalized use of a basic logistic function, \( x(1-x) \), which is customarily exploited to depict the case of population growth. It consists of the two essential but counteracting parts, the first responsible for mortality, \( x \equiv \alpha^n \), (i.e., reactant disappearance and the product formation) and the other for fertility, \( (1-x) \equiv (1 - \alpha)^p \) (i.e., a kind of products’ hindrance generally accepted as an ‘autocatalytic’ effect). The non-integral exponents, \( m \) and \( n \), play thus the role similar to all circumstances, which act for the true fractal dimensions.

Peculiarity of non-isothermal approach

For all generally assumed transformations, the most frequently applied isothermally derived theories are directly applicable to non-isothermal kinetic evaluations. A more detailed analysis imposes, however, that such a non-isothermal generalization is only possible along the lines of the so-called ‘isokinetic’ hypothesis, i.e., the invariance of the rate equation under any thermal conditions. It was shown that the non-isothermal derivation includes the operation of integrated Arrhenius exponential, i.e., the so called \( p(x) \) function. Application of suitable approximations lead to the change of the pre-exponential factor only maintaining thus the residual model function unchanged. Thanks to such coincidence, all functions tabulated above are applicable for a straightforward submission to kinetic evaluations under non-isothermal conditions.

So-called integral methods of evaluation became rather widespread due to its apparent simplicity. They are based on a modified, integrated form of the function \( f(\alpha) \), which is determined by the following relation, \( g(\alpha) = \int_0^1 f(\alpha) \ d\alpha = T_0 \int k(T) \ dT/\phi = (AE)/(\phi R) \ \exp(-E/RT) \ \pi(x)/x = (AE)/(\phi R) \ p(x) \), where \( \phi \) is the constant heating rate applied, \( \pi(x) \) is an approximation of the temperature integral (often used in the intact representation as the \( p(x) \) function, where \( x = E/RT) \). There are many approximations of this temperature integral arising from the simplest \( \pi(x) = 1/x \) and \( (1-2x)/x \) (based on the expansion) to more accurate \( \pi(x) = 1/(x+2) \) up to the most sufficient \( \pi(x) = (x+4)/(x^2 + 6x + 6) \) (based on the rational approximations). However, the determination and sufficiently precise calculation of the \( p(x) \) function should be seen as a marginal problem though it has led to exceptionally wide publication activity. Despite the specific accounts on \( p(x) \) accuracy it can be shown that the mathematical nature tends to simple solutions, because in most kinetic calculations the effect of the actual value (of \( \pi(x) \) and/or \( p(x) \)) is often neglected or, at least, greatly diminished. This factually implies that \( k(T) \) is (often unintentionally) considered as a constant and, instead of complex integration, is simply withdrawn in front of the integral, namely: \( \int k(T) \ dt \approx k(T) \ \int dt \), which handling is habitually obscured within complicated mathematics (often associated within \( p(x) \) deciphering).

It is worth highlighting that already a plain application of a logarithmic function brings not only the required data smoothing but also introduces a higher degree of insensitiveness. For that reason, the popular double-logarithmic operation effectively paralyses the methods’ discriminability
towards individual kinetic models as well as our attached desire to attain as linear proportionality as possible. We may humorously make a note of curious but sometimes actual role of double-logarithmic plotting in sense of a drawing on ‘rubber-stretch’ paper.

To get a better insight, we can divide the so called integral methods into three groups according to the method of plotting $\ln g(\alpha)$ against the three possible temperature functions (i.e., $\ln T$, $T$ or $1/T$) giving thus the respective slopes of $\tan \alpha$. Consequent estimation of $E$ depends on the respective values, i.e., $RT_n (\tan \alpha - 1)$, $RT_n^2 \tan \alpha$ and/or $(RT_n \alpha - 2RT)$. The involved approximation can be tested using the asymptotic expansion of a series with a dimensionless parameter replacing E. It can be seen that the latter dependence is twice as good as that of the former two dependencies. In this way, we can confirm the numerical results of several authors who found that the plain dependence of $\ln g(\alpha)$ vs. $T$ yields $E$ with an error of about 15% at best, whereas the $\ln g(\alpha)$ vs. $1/T$ plot can decrease the error by half. This is relative to the entire series given by set of $T$’s and $1/T$’s.

Another obstruction may be seen when employing a more general temperature program, which is proportional to the reciprocal temperature, i.e., $dt = \phi \, d(1/T)$. In this case the function $p(x)$ simplifies in the form of a difference $dT$, which can be replaced by $d(1/T)$ so that $p(x) \sim (ZE/R\phi) [(-E/R)(1/T - 1/T_0)]$, which would be no complication but, on contrary, it would have allowed a more straightforward kinetic appraisal. Although such temperature regulation is rare, it would essentially facilitate the kinetic data calculation, requiring, however, another systematic. It would be feasible, depending just on the manufacturers’ will, as to consider somehow unproblematic extension of their commercially available digital programmers to become applicable for another, newly specified case of kinetic investigations.

Often neglected but one of the most important cases is the assumption of differences arising from the effect of changing the equilibrium background of the process. It can be illustrated on the example of various processes taking place in non-stoichiometric oxides (e.g. tetragonal-cubic phase transformation of spinels: $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ (t) $\rightarrow$ $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ (c)). The simple kinetic analysis of plotting the model relation against reciprocal temperature revealed that the change of the slope, often ascribed to the change of reaction mechanism, is just caused by switching between the part of the process proceeding under changing equilibrium background and the remainder invariant part controlled by the process itself.

Proximity to equilibrium plays an important but often underestimated role, which is effective in the beginning of a reaction where the driving force is minimal. In such a case some integration terms of $p(x)$–function cannot be neglected as conventionally accomplished in most kinetic studies. The resulting function $[p(x) - p(x)]$ is more complex and the associated general plot of $g(\alpha)$ vs. $1/T$ develops into non-linearity. This consequence can be best illustrated on the decomposition of $\text{CaCO}_3$ as an habitually misconducted case.

**KINETIC EVALUATION PROCEDURES**

Distinctiveness graph below of the model functions of $\ln f(\alpha)$ vs. $\alpha$ shows three characteristic areas of self-similar models abbreviated as nucleation (A), phase-boundary (R) and diffusion (D) controlled processes. The middle plot displays the wider variety of possible diffusion-paths controlled processes exhibiting a non-integral (fractal $\{(1-D)/D\}$) geometry. On the left-upper shaded areas depict the models formed on basis of the strict Euclidean geometry. However, the models involve a modified course of characterization, which allows intermediate cases to exist (e.g. for $2<D<3$ it holds $d\alpha/dt = \{(1-\alpha)^{(1-D)/D}-1\}^{-1}$). Such approach seemingly enables to cover a larger area with the array of kinetic curves making possible their increased packing, e.g., from $D=2$, which coincides with the classical $D_2$ curve (shown in the left graph), we can see the curves’ shift to the upper side of the plot with increasing D’s as far as to 1.9 and then their moving downwards from $D=2.1$ to 3.0 to crowd the normally unfilled area (defined between the conventional $D_2$ and $D_4$ curves). The same curve swelling applies to the other groups (A’s and R’s, see left) and it shows well the almost meaningless attempt to define precisely the solitary particularity of individual reaction as introduced by Riko Ozao (Kanagawa, Japan). Right is the characteristic graph of $z(\alpha) =$
The parameters occurring in both functions are only certain perceived quantities (similarly to the above portrayal of ‘apparentness’), which, in general, possess no mechanistic interpretation. Such values are composite and their representation in terms of individual sub-processes and associative subordinated values can be found obscure. Since \( k(T) \) is not the standard rate constant, there is no reason to be restricted by an exponential relationship and thus other functions can be used leading to a closed form of the temperature integral.

This single-step kinetics approximation involves the imperative condition of separability of both temperature and conversion functions and any couple of such autonomous functions lead to an acceptable description of accommodating kinetics. However, it has been reasoned that if a couple of separable functions cannot be found, it indicates that the single-step kinetics approximation is too crude and the description of the kinetic hypersurface may become inappropriate. The temperature and conversion functions contain enough adjustable parameters so that their values are attuned in the procedure of fitting in order to reach the best fit between the experimental and calculated data. The
separability of temperature and conversion functions must thus imply that the values of adjustable parameters are supposed to be unvarying in the whole range of conversions and temperatures.

It is generally recognized that the isoconversional methods lead to the dependence of adjustable parameters in the temperature function on conversion. This fact has provided the concept of a variable activation energy. As shown in, dependence of activation energy on conversion violates the conditions separability and thus, in the case of variable activation energy, the basic assumption of the single-step kinetics approximation is incompetent for the associated description and calculated data are inadequate. This factually represents the “logical trap” of the concept of variable activation energy since it becomes mathematically incorrect and inherently self-inconsistent. Deductions drawn from the dependence of activation energy on conversion can hardly be considered trustworthy and should be judged very critically and carefully.

We should accentuate again that the main contribution of the above concept of single-step kinetics approximation is to elucidate the non-physical meaning of equations involved so that it is just a mathematical tool enabling a description of the kinetics of solid-state reactions without any deeper insight into their mechanism. The correct mathematical description should recover the values of conversion and the rate of the reaction under study for given values of time and temperature. Since the adjustable parameters represent just apparent quantities, no conclusions should be drawn from their values and so it is close to the use of fractal power exponents discussed beforehand but some useful conclusions can be drawn from the values of reaction rates or isoconversional temperatures and times such as it has been done in the study of induction periods.

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COMPARISON OF CRYSTALLIZATION KINETICS DETERMINED BY ISOTHERMAL AND NON-ISOTHERMAL METHODS

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ABSTRACT

Theoretical results for nucleation and growth controlled transformations indicate that a non-isothermal generalization is only possible along the lines of the isokinetic hypothesis, i.e., the invariance of the rate equation under any thermal conditions. The alternative formalism, i.e., the general use of the isothermal law and the corresponding modification of the rate equation under non-isothermal conditions, is found to be incorrect. Different methods for the evaluation of kinetic parameters are compared, taking into account even thermal lag corrections.

It is illustrated by experimental results for oxide, chalcogenide and metallic glasses that all of the non-isothermal methods that yield kinetic parameters in good agreement with the appropriate isothermal results are easily derived from the usual rate equation.

INTRODUCTION

The crystallization of different glassy materials has been extensively investigated by various non-isothermal methods. It is evident that the kinetics of crystallization are important from the points of view of both fundamental and applied research. The theory and practice of this evaluation, however, are far from being universally accepted.

The general question of whether the usual rate equation is applicable to non-isothermal studies [1–5] is also relevant for crystallization. Apparently unrelated to this problem, many researchers [6–10] freely applied the equations derived for the isothermal case by Johnson and Mehl, Avrami, Kolmogorov and Yerofeev to non-isothermal conditions. When the time derivative of these JMAKY kinetics were calculated, new methods were suggested [11–13] for the calculation of kinetic parameters that are significantly different from those generally applied. Despite a detailed criticism of
these attempts [14–32], the exact mathematical equivalence of the modified rate equation and the use of isothermal laws under non-isothermal conditions were not generally recognized [33,34].

In this paper, some results on the theory of nucleation and growth controlled transformation are reviewed to show that a non-isothermal generalization is only possible along the lines recommended by the isokinetic hypothesis, i.e., the invariance of the rate equation. If this treatment is to be believed, however, it must be shown that those evaluation methods which claim good experimental verification are consistent with this framework even if originally suggested on the basis of now obsolete theories.

THEORY OF NUCLEATION–GROWTH KINETICS UNDER GENERAL THERMAL CONDITIONS

Crystallization is a special case of the nucleation and grain growth controlled solid-state transformation processes, the theory of which is well known [35–38]. If an embryo of the transformed phase nucleates at moment \( \tau \) and grows thereafter isotropically in three dimensions with a linear momentary growth rate \( Y(t') \) in moment \( t' \), then its volume \( v \) at moment \( t \) (where \( \tau < t' < t \)) is

\[
v(\tau, t) = \frac{4\pi}{3} \left[ \int_\tau^{t'} Y(t') \, dt' \right]^3
\]

(1)

When the possible overlap of the grains is neglected, the so-called extended volume \( V_{\text{ext}} \) is calculated:

\[
V_{\text{ext}} = V \left[ N_0 v(0, t) + \int_0^t I(\tau) v(\tau, t) \, d\tau \right]
\]

(2)

where \( N_0 \) is the initial number of nuclei and \( I = I(\tau) \) is the nucleation rate per unit volume. As the change of the real transformed volume, \( dV_t \), and that of the extended volume, \( dV_{\text{ext}} \), is related by

\[
dV_t = \left( 1 - \frac{V}{V_{\text{ext}}} \right) dV_{\text{ext}}
\]

(3)

the basic nucleation-growth equation for the transformed fraction \( \alpha = V_t / V \) is

\[
-\ln(1 - \alpha) = \frac{4\pi}{3} \left( N_0 \left[ \int_0^t Y(t') \, dt' \right]^3 + \int_0^t I(\tau) \left[ \int_\tau^{t'} Y(t') \, dt' \right]^3 \, d\tau \right)
\]

(4)

This equation is evidently valid under any thermal conditions. Up to this point no assumptions have been made regarding the origin of the time dependence of \( I \) and \( Y \), so it could easily include also the implicit time dependences \( Y[T(t')] \) and \( I[T(\tau)] \). An important limitation of this equation, however, stems from the use of eqn. (3), which describes a completely
random overlap of growing crystallites. Surface crystallization is a clear case
where this assumption must not be valid. Owing to the possible absence of
overlap, this case is also easily treated even under general thermal condi-
tions.

For any shape where the volume is expressed as the product of a
dimensional factor and the cube of a characteristic distance, the calculation
easily yields

\[ 1 - (1 - \alpha)^{1/3} = \int_0^{t_f} k[T(t')]dt' \]  

which is a clear example of \( n \)th order chemical reaction kinetics. Having
established that the classical methods of kinetic parameter evaluation are to
be used in this instance, we might return to our central problem: evaluation
of kinetic parameters based on eqn. (4).

The two terms in eqn. (4) determine the two limiting processes of major
interest under isothermal conditions when \( Y = \) constant:

(a) the growth of frozen-in nuclei (\( N_0 \neq 0 \)) without thermal nucleation
\( (I=0) \):

\[ [ -\ln(1 - \alpha) ]^{1/3} = kt \]  

(b) homogeneous thermal nucleation (\( N_0 = 0 \), \( I = \) constant \( \neq 0 \)):

\[ [ -\ln(1 - \alpha) ]^{1/4} = kt \]  

It is worth noting that in a number of instances, e.g., for the time-depen-
dent transient nucleation where \( I(\tau) = I_0 e^{-\tau/\tau_0} \) or for the diffusion-limited
growth where the characteristic distance is proportional to \( t^{1/2} \), a form
analogous to eqns. (6) and (7):

\[ [ -\ln(1 - \alpha) ]^{1/n} = kt \]  

holds as an acceptable approximation [39], where the exponent \( n \) gives an
indication of the mode of transformation. This is the physical background of
the wide applicability of the JMAKY equation under isothermal conditions.

The same treatment is also applicable to the non-isothermal case taking
into account that now

\[ Y(t') = Y_0 e^{-E_s/RT(t')} \]  

The generalization of case (a) is very easy, yielding

\[ [ -\ln(1 - \alpha) ]^{1/3} = \int_0^{t_f} k[T(t')]dt' \]  

where

\[ k(T) = Z_e e^{-E_s/RT} \]  

\[ Z_e = Y_0 (4\pi N_0/3)^{1/3} \]
For case (b) the calculation has already been carried out [40,41] by evaluating the double integral in eqn. (4) by the usual methods, where \( T = T_0 + \beta t \)
\[
I(\tau) = Z_ne^{-E_n/RT(\tau)}
\]
The result is
\[
[-\ln(1 - \alpha)]^{1/4} = \bar{Z}(Z_n, Z_g, E_n, E_g) \frac{\bar{E}}{\beta R} \left( \frac{RT}{E} \right)^2 e^{-\bar{E}/RT} = \int_0^t \tilde{k}[T(t')] dt'
\]
where
\[
\bar{E} = \frac{(E_n + 3E_g)}{4}
\]
\[
\tilde{k} = \bar{Z}e^{-\bar{E}/RT(t)}
\]
It should be clear from eqns. (10) and (14) that the non-isothermal equivalent of the widely used isothermal JMAKY relation [eqn. (8)] is
\[
[-\ln(1 - \alpha)]^{1/n} = \int_0^t k'[T(t')] dt'
\]
as also shown by Henderson [42,43] and Meisel and Cote [44]. Some particular points following from the preceding analysis are worth noting:

(A) The time derivatives of eqns. (8) and (17) are the same, i.e., the rate equation
\[
\frac{d\alpha}{dt} = n\bar{Z}(1 - \alpha) \left[ -\ln(1 - \alpha) \right]^{n-1} e^{-\bar{E}/RT}
\]
beats the same form for both isothermal and dynamic cases.

(B) The isothermal transformed fraction can naturally be written either as
\[
\alpha = 1 - e^{-(kt)^n}
\]
(19a)
or as
\[
\alpha = 1 - e^{-kt^n}
\]
(19b)
as the two equations use only a different definition of the activation energy. If
\[
k = k_0e^{-E/RT}
\]
(20a)
and
\[
k_* = k_0*e^{-E_*/RT}
\]
(20b)
then
\[
E_* = nE
\]
(21)
However, the frequently used [45,46] differential form
\[
\frac{d\alpha}{dt} = k_* n(1 - \alpha)t^{n-1}
\]
(22)
is not valid \[51,52\], as

\[-\ln(1 - \alpha) = \left( \int_{0}^{t'} k[T(t')] dt' \right) = \int_{0}^{t'} k[T(t')] t'^{n-1} dt' \] (23)

This fact was originally observed by De Bruijn et al. \[40\] and was recently re-emphasized by Louis and Garcia-Cordovilla \[47-49\] and by Kasap and Yuhasz \[108\]. The correct form of eqn. (22) where the rate equation is formulated as a function of \( T \) and \( \alpha \) only is expressed as \[51,52\]

\[\frac{d\alpha}{dt} = nk^{1/\alpha}(1 - \alpha)\left[ -\ln(1 - \alpha) \right]^{n-1} \] (24)

Later we shall return to establish that this freedom in defining the activation energy does not influence the comparison of isothermally and non-isothermally determined kinetic parameters.

(C) It is evident from eqn. (17) that the isothermal form of the JMAKY relation [eqn. (8)] is not valid under non-isothermal conditions. The relationship derived [eqn. (17)] clearly shows that \( \alpha \) depends on the whole \( T(t) \) path. In this way the theory of nucleation and growth controlled transformation is completely incompatible with the existence of an \( \alpha = \hat{\alpha}(t, T) \) function that would predict \( \alpha \) if only the end-point \( (t, T) \) is specified, i.e., with the assumption that we shall call the alternative formalism.

The fact that the transformed fraction is a path function does not give any problems when \( \alpha \) is determined for a properly defined thermal route. For example, with linear heating \[50-52\]

\[T = T_0 + \beta t\]

Equation (17) yields

\[g(\alpha) = [ -\ln(1 - \alpha)]^{1/n} = \frac{ZE}{\beta R} p(E/RT) \] (25)

where \( p(E/RT) \) denotes the exponential integral. Equation (25) is no doubt a functional relationship, i.e., for linear heating the \( \alpha = \hat{\alpha}_{\text{th}}(\beta, T) \) function exists.

In this way the theory of nucleation and growth controlled transformations makes an unambiguous choice between the two methods of kinetic parameter evaluation. The usual method is based on the isokinetic hypothesis, i.e., on the invariance of the rate equation

\[\frac{d\alpha}{dt} = k(T)f(\alpha) \] (26)

under any thermal conditions. The transformed fraction is

\[g(\alpha) = \int_{0}^{\alpha} \frac{d\alpha'}{f(\alpha')} = \int_{0}^{t'} k[T(t')] dt' \] (27)

which yields \( g(\alpha) = kt \) only under isothermal conditions. This hypothesis,
even if not exactly valid [43] (causing here only a deviation of $\bar{Z}$ from its isothermally calculated value), is a reasonable approximation also in our case.

The alternative formalism is based on the existence of an $\alpha = \hat{\alpha}(T, t)$ function. A significant modification of the rate equation is calculated under non-isothermal conditions [1–5]. The preceding analysis therefore excludes the applicability of this formalism to nucleation and growth controlled transformations. The exact mathematical equivalence of the modified rate equation and the use of the isothermal law under non-isothermal conditions [6–10] will be shown in a separate paper [34].

EVALUATION OF KINETIC PARAMETERS FROM THERMOANALYTICAL EXPERIMENTS

The evaluation of linear heating experiments is based on eqn. (25), where two different approximations of the exponential integral, namely the Doyle approximation

$$l_{\text{Doyle}}(E/RT) = \ln p(E/RT) \approx -5.33 - 1.05 \frac{E}{RT} \pm 3\%$$  \hspace{1cm} (28)

and the asymptotic equation

$$p\left(\frac{E}{RT}\right) = e^{-E/RT}\left(\frac{RT}{E}\right)^2\left[1 - \frac{2RT}{E} + \sigma \left(\frac{RT}{E}\right)^2\right]$$  \hspace{1cm} (29)

will be used. The first term in eqn. (29) means typically a few per cent accuracy of $p(E/RT)$. It should be understood, however, that the use of eqn. (28) for estimating $p(E/RT)$ itself is irrelevant, as the 3% error in the exponent has very serious consequences, as shown in Table 1.

This is why the form of the rate equation proposed by Matusita et al. [53]:

$$\frac{d\alpha}{dt} = K(1 - \alpha)\beta^n \exp\left(-1.05 \frac{E}{RT} m\right)$$

is considered to be too rough an approximation to be recommended. The actual evaluation methods proposed [53], however, utilize only $\ln(da/dt)$

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect of a 3% error in the Doyle equation for calculating $p(E/RT)$</td>
</tr>
<tr>
<td>$l_{\text{Doyle}}(E/RT) = -5.33 - 1.05(E/RT)$; with an error of ±3%, and $E/RT = 40$</td>
</tr>
<tr>
<td>$\ln p(E/RT)$</td>
</tr>
<tr>
<td>$p(E/RT)$</td>
</tr>
<tr>
<td>$p/p_{\text{equation}}$</td>
</tr>
</tbody>
</table>
and \( \ln g(\alpha) \) and in this way are also easily derived in the correct formalism: when the logarithm of eqn. (25) is connected with eqn. (28), then

\[
\ln[-\ln(1-\alpha)] \approx n \ln \frac{Z}{\beta} - 1.05 \frac{nE}{RT} + C
\]

results. If the logarithm of eqn. (18) is combined with either eqn. (28) or (29), then the result is [54]

\[
\ln \frac{d\alpha}{dt} = \ln \frac{Z^n}{\beta^{n-1}} - \frac{nE}{RT} + \sigma \left(1 - \alpha, \ln \frac{T}{T_0}\right)
\]

It is evident that these plots might reveal only \( nE \). If \( n \) and \( E \) are to be determined separately from a single thermogram, then the three-term version of eqn. (29) is applied to yield

\[
\ln \left[-\ln \left(\frac{1-\alpha}{T^2}\right)^{1/n}\right] = \ln \left[\frac{ZR}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}
\]

The separate determination of \( n \) and \( E \) in this way requires a very high precision if the variation of terms whose order of magnitude is \( \ln T \) (found to be almost negligible with the usual precision) is to be significantly established in addition to terms of the order of \( 1/T \).

As the typical variations are \( \partial (1/T)/1/T = \partial T/T \approx 10\% \) and \( \partial \ln T/\ln T \leq 2\% \), and the precision of \( \alpha \) itself can hardly surpass \( 2\% \), the fulfillment of this requirement is far from trivial. This is why multi-thermogram methods, usually based on temperature shifts caused by a variation of the heating rate, \( \beta \), play a dominant role. It is a basic advantage of these methods that the determination of activation energy (as it is defined here) is independent of the transformation mechanism [50,55–59]. The connection of eqn. (25) with eqn. (28) for any \( g(\alpha) \) and for any \( \alpha_0 \) fixed transformed fraction yields

\[
\ln \left[\frac{\beta}{Z}\right] = C_1 - 1.05 \frac{E}{RT_{\alpha_0}}
\]

while the use of eqn. (29) results in

\[
\ln \frac{\beta}{ZT_{\alpha_0}^2} = C_2 - \frac{E}{R} \frac{1}{T_{\alpha_0}}
\]

where \( C_1 \) and \( C_2 \) are independent of \( \beta \) and \( T_{\alpha_0} \), which denotes the temperature where the transformed fraction is \( \alpha_0 \). If \( Z = \text{constant} \) it is incorporated in the \( C \) coefficient and then these equations are the Ozawa and the Kissinger plots, respectively, which are seen here to be only different approximations of \( p(E/RT) \) and are thus equivalent [60]. It is also easily verified that the transformed fraction at the maximum transformation rate, \( \alpha_m \), is independent of \( \beta \) and is thus useful for the determination of
activation energy without integrating the thermoanalytical curve. The usual criticism that the thermal lag between \( \frac{d\alpha}{dt} \) and the measured \( \Delta T \) invalidates this method will be treated in the Appendix and will be shown to be inapplicable to modern thermoanalytical instruments. Using

\[
\frac{d\alpha}{dt} = \frac{Z}{\beta} e^{-E/RT} f(\alpha) \tag{35}
\]

the maximum condition is

\[
\frac{d}{dT} \left( \frac{d\alpha}{dT} \right)_{\alpha_m} = 0 = \left[ e^{-E/RT} \frac{df(\alpha)}{d\alpha} \frac{d\alpha}{dT} + \frac{E}{RT^2} e^{-E/RT} f(\alpha) \right]
\]

where the substitution of eqn. (35) and rearrangement yields

\[
\frac{ZE}{R\beta} \left( \frac{RT}{E} \right)^2 e^{-E/RT} \left. \frac{df(\alpha)}{d\alpha} \right|_{\alpha_m, T_m} + 1 = 0
\]

which is reduced with the help of the first term approximation in eqn. (29) to

\[
g(\alpha) \left. \frac{df(\alpha)}{d\alpha} \right|_{\alpha_m} + 1 = 0
\]

This relationship, besides proving that \( \alpha_m \) is independent of \( \beta \) for any process described by eqns. (26) and (27), is also applicable to the direct determination of \( \alpha_m \) with

\[
f(\alpha) = n (1 - \alpha) \left[ -\ln(1 - \alpha) \right]^{n-1} \tag{36}
\]

\[
g(\alpha) = \left[ -\ln(1 - \alpha) \right]^{1/n} \tag{37}
\]

functions, yielding

\[
\alpha_m = 1 - \frac{1}{e} = 0.63 \tag{38}
\]

These results, which were also derived previously [42,61–63], show that statements sometimes found in the literature that “the linearity of the Kissinger plot shows the applicability of the first-order kinetics” [106] or “the Ozawa plot is valid for chemical reactions only” [107] are not substantiated and the shift of \( \alpha_m \) with \( \beta \) which is also sometimes discussed [23a] must be insignificantly small.

The maximum reaction rate is calculated as

\[
\left. \frac{d\alpha}{dt} \right|_{\text{max}} = \frac{nZ}{e} e^{-E/RT_m} \tag{39}
\]

which is clearly different from the result derived for fixed \( n \)th-order chemical kinetics, cf. eqn. (26), where \( f(\alpha) = (1 - \alpha)^n \) and

\[
\left. \frac{d\alpha}{dt} \right|_{\text{max}} = - \frac{E}{RT_m^2} (1 - \alpha)/n
\]
These results, i.e., for transformations described by eqns. (18) and (25) under linear heating conditions: (a) $\alpha_m = 0.63$ (independent of $\beta$, $n$ or any other parameters), (b) $T_m$ is independent of $n$ [which follows directly from eqn. (25) by applying point (a)] and (c) the maximum reaction rate is directly proportional to the characteristic exponent, $n$, are also fully confirmed by a detailed numerical simulation [64].

A comparison of isothermal and non-isothermal temperature shift methods is appropriate here. As eqn. (26) is established to be valid in both cases, the relation

$$\ln \left. \frac{d\alpha}{dt} \right|_{\alpha_0} = \ln \left( Zf(\alpha_0) - \frac{E}{RT} \right)$$

(40)

is applicable. In addition, the condition for the maximum isothermal rate is

$$k_{t_m} = \left( \frac{n-1}{n} \right)^{1/n}$$

(41)

which is independent of $T$, i.e., $\alpha_m$ is used in eqn. (40) under any circumstances. On the other hand the relationship evident from eqn. (8):

$$\ln t_{\alpha_0} = C - \frac{E}{RT}$$

(42a)

is also valid with $t_m$. All of these relationships predict the same activation energy that is obtained by eqns. (33) and (34) under non-isothermal conditions. It is evident that a different activation energy can also be defined by eqn. (19b). By this definition the isotherms

$$\ln t_m = \tilde{C} + \frac{E_*/nRT}{n}$$

(42b)

result, but owing to eqn. (24) the relationships (33) and (34) also yield $E_*/n$ in this instance.

This section should be concluded by emphasizing that peak methods, in addition to being so useful and convenient, also give a significant loss of information. With the availability of cheap microcomputers it is advisable to evaluate the full thermoanalytical curve to establish that the same activation energy is really associated with any transformed fraction value, the assumed transformation mechanism is in fact valid and the same characteristic exponent is determined from different heating rate experiments. If these cross-checks are carried out successfully then a series of different heating rate curves can give as reliable a characterization as a series of different temperature isotherms, while $\alpha$ and $d\alpha/dt$ might be determined with better accuracy even faster and the problems of the initial transient and the difficult determination of the incubation time are better avoided. This means that non-isothermal measurements can be used even for the determination of the mechanism of crystallization, in contrast to the belief that it is restricted to isothermal methods only.
EXPERIMENTAL RESULTS FOR THE CRYSTALLIZATION KINETICS OF DIFFERENT GLASSES

This paper does not attempt to cover the vast literature on crystallization. Some results on oxide, chalcogenide and metallic glasses are mentioned to reveal how and why the general methods outlined in the previous section are modified under special circumstances and to investigate whether the same kinetic parameters are indeed to be determined from isothermal and non-isothermal experiments.

Oxide glasses

A basic feature of oxide glasses is the separation of temperature ranges for nucleation and growth. Thermal experiments detecting heat evolution naturally observe the growth of pre-existing nuclei. If the glasses were heated uniformly in the nucleation temperature range and investigated later with different heating rates in the growth regime only, then the evaluation methods in the previous section can be used without any modifications. As the samples are usually heated at the same rate in both regimes they are not even equivalent before crystallization and therefore a modification arises

The number of nuclei is described as [68]

\[ N_0 = N_1 + N_2 + N_3 \]  

where \( N_1 \) is the number of bulk nuclei initially present, \( N_2 \) is that of nucleated during heating in the appropriate temperature range and \( N_3 \) is the number of surface nuclei treated separately. If \( N_1 \gg N_2 \) ("nucleated glass") then \( N_0 \approx N_1 \) is independent of \( \beta \) and the usual equations can be used. If \( N_1 \ll N_2 \) ("as-quenched glass"), then

\[ N_2 = \int_{T_1}^{T_2} I(T) dt = \frac{1}{\beta} \int_{T_1}^{T_2} I(T) dT = \frac{N_0}{\beta} \]  

where \( T_1 \) and \( T_2 \) are the lower and higher limits of the nucleation temperature range, respectively, and crystallization is observed at \( T > T_2 \). Under these circumstances

\[ N_0 \approx N_2 = \frac{N_0}{\beta} \]  

and through eqn. (12)

\[ \mathcal{Z} \approx \beta^{-1/n} \]  

is obtained, which modifies eqns. (30)–(34) to

\[ \ln[-\ln(1-\alpha)] = -(n+1) \ln \beta - 1.05n \frac{E}{RT} + C \]  

(47)
Surface nucleation was shown to follow fixed-order chemical kinetics [eqn. (5)] and therefore an apparent order \( n - 1 \) is expected here.

The applicability of these relationships was carefully tested for LiO\(_2\) - 2SiO\(_2\) glasses [53,69–73]. It was verified that \( \ln[-\ln(1 - \alpha)] \) vs. \( \ln \beta \) with \( T = \) constant yields ca. 3 and ca. 4 for the nucleated and as-quenched glass, respectively [eqn. (30) with \( Z = \) constant and eqn. (47)] [53]. It was also established that the activation energies determined from eqns. (33) and (49) are in good agreement with that of viscous flow. Similar agreement is also reported for the surface nucleated case [72,73], where the exponent \( n = 1 \) is observed. (Correspondence of the activation energies of surface and bulk crystallization was also verified for metallic glasses [74].) These results are also substantiated by independent observations [75,76]. Equations (30)–(34) are also found to be applicable to the crystallization of CaO–SiO\(_2\) based glasses [77,78] and good agreement with isothermal values was reported for GeO\(_2\) and 3BaO·5SiO\(_2\) also [79].

In the original publications [53,68,69–73,75–79], eqns. (30)–(34) and (47)–(50) were derived by an irregular procedure, either assuming the validity of the JMAKY kinetics [eqn. (8)] under non-isothermal conditions, or using the extremely rough \( e^{(E/(RT))} \approx p(E/RT) \) approximation. These doubtful procedures do in fact lead to some ambiguous results, e.g., to the suggestion of an evaluation method for DDTA curves [8] that is not yet derived from correct principles [29] and to a modified exponent in eqn. (50) where \( T_{a_0}^2 \) is calculated instead of the correct \( T_{a_0}^{2n} \). This latter problem is irrelevant, however, as the variation of \( \beta \) is dominant and in fact both methods, eqns. (49) and (50), yield to a good approximation the same \([n/(n + 1)](E/R)\) value [73].

It is emphasized here that eqns. (30)–(34) and (47)–(50) have now calculated from correct premises [63] and found to be experimentally applicable in some instances. The basic reason for the modification apparent in eqns. (47)–(50) should, however, be understood: it is only a correction due to the unequal heating rates applied in the nucleation range, resulting in samples with unequal kinetic parameters.

**Metallic glasses**

For metallic glasses the difference between the glass transition temperature, \( T_g \), and that of crystallization, \( T_{cr} \), is very small; in many instances \( T_g \)
is not even observed, being overlapped by $T_{cr}$. Under these circumstances a separate temperature regime for nucleation cannot be defined. A general equation for the activation energy was suggested by Von Heimendahl and co-workers [80–82]

$$
\bar{E} = \frac{aE_n + bmE_g}{a + bm}
$$

(51)

where $a = 0$ for quenched-in nuclei and $a = 1$ for a constant isothermal nucleation rate, $m$ is the number of growth dimensions and $b = 1$ for linear and $1/2$ for parabolic growth. The activation energies of nucleation, $E_n$, and growth, $E_g$, were separately determined by transmission electron microscopy, and $\bar{E}$ predicted by eqn. (51) was in good agreement with that determined by the usual methods. As a high value is obtained for $E_n$, it is evident that changes in the concentration of the quenched-in nuclei significantly influence $\bar{E}$. The effect of quenching rate on crystallization has been experimentally verified for a series of Fe–B glasses [89]. This fact makes the

### TABLE 2

Comparison of activation energies determined by isothermal and non-isothermal methods

<table>
<thead>
<tr>
<th></th>
<th>Isothermal</th>
<th></th>
<th>Non-isothermal</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eqn.</td>
<td>Ref.</td>
<td>$E$(kJ mol$^{-1}$)</td>
<td>Eqn.</td>
</tr>
<tr>
<td>Fe$<em>{90}$P$</em>{10}$C$_{7}$</td>
<td>42</td>
<td>83</td>
<td>435</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{90}$Ni$</em>{40}$P$<em>{14}$B$</em>{3}$Si$_{3}$</td>
<td>42</td>
<td>84</td>
<td>426</td>
<td>33</td>
</tr>
<tr>
<td>Fe$<em>{90}$Ni$</em>{36}$Cr$<em>{14}$P$</em>{12}$B$_{6}$</td>
<td>42</td>
<td>86</td>
<td>286</td>
<td>33</td>
</tr>
<tr>
<td>Fe$<em>{90}$Ni$</em>{40}$P$<em>{14}$B$</em>{3}$</td>
<td>42</td>
<td>85</td>
<td>376</td>
<td>33</td>
</tr>
<tr>
<td>Fe$<em>{90}$B$</em>{25}$</td>
<td>42</td>
<td>84</td>
<td>385</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{90}$B$</em>{90}$</td>
<td>42</td>
<td>89</td>
<td>239</td>
<td>34</td>
</tr>
<tr>
<td>Fe$<em>{90}$B$</em>{90}$</td>
<td>19a</td>
<td>93</td>
<td>240–245</td>
<td>34</td>
</tr>
<tr>
<td>Fe$<em>{90}$Co$</em>{18}$Si$<em>{1}$B$</em>{14}$</td>
<td>42</td>
<td>96</td>
<td>231</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>360</td>
<td></td>
</tr>
<tr>
<td>Co$<em>{44}$P$</em>{15}$</td>
<td>42</td>
<td>94</td>
<td>195</td>
<td>34</td>
</tr>
<tr>
<td>Co$<em>{44}$P$</em>{18}$</td>
<td>42</td>
<td>94</td>
<td>190</td>
<td>34</td>
</tr>
<tr>
<td>Ni$<em>{44}$P$</em>{15}$</td>
<td>19</td>
<td>44</td>
<td>221</td>
<td>34</td>
</tr>
<tr>
<td>Pd$<em>{90}$Ge$</em>{20}$</td>
<td>42</td>
<td>90</td>
<td>212</td>
<td>34</td>
</tr>
<tr>
<td>(Au$<em>{85}$Cu$</em>{15}$)$<em>{77}$Si$</em>{8}$Ge$_{14}$</td>
<td>42</td>
<td>91</td>
<td>250</td>
<td>34</td>
</tr>
<tr>
<td>Zr$<em>{75}$P$</em>{25}$</td>
<td>40</td>
<td>95</td>
<td>339</td>
<td>34</td>
</tr>
<tr>
<td>Ni$<em>{40}$Nb$</em>{40}$</td>
<td>42</td>
<td>92</td>
<td>629</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>433</td>
<td></td>
</tr>
<tr>
<td>Al$<em>{75}$Te$</em>{77}$</td>
<td>40</td>
<td>100</td>
<td>270</td>
<td>34</td>
</tr>
<tr>
<td>(Ge$<em>{2}$Sb$</em>{2}$)$<em>{70}$(GeTe)$</em>{30}$</td>
<td>40</td>
<td>99</td>
<td>176</td>
<td>34</td>
</tr>
</tbody>
</table>

*a* Refined Ozawa plot [59] for different transformed fractions and detailed analysis of the full $d\alpha/dt$ curve [65–67].

*b* Different stages of the transformation evaluated separately.

*c* Transformed fraction determined from electrical resistance.
comparison of results obtained on different ribbons very difficult and can even contribute to the significant dispersion obtained on different batches of nominally similar samples [88]. Despite these difficulties, there are many examples in the literature where an acceptable agreement was observed between activation energies obtained by isothermal and non-isothermal methods (Table 2). It is only remarked here that agreement is found both for metallic and chalcogenide glasses and for a wide variety of $a$ and $b$ parameters. $n \approx 3$ is observed for Fe$_{75}$B$_{25}$ and $n \leq 3$ is established for Fe$_{80}$B$_{20}$, which indicates the dominant role of the quenched-in nuclei. On the other hand, $n \geq 4$ is found for Fe$_{40}$Ni$_{40}$P$_{14}$B$_{6}$, which indicates linear growth with concurrent nucleation, whereas parabolic growth is applicable to Fe$_{32}$Ni$_{36}$Cr$_{14}$P$_{12}$B$_{6}$ [80].

There are only a few instances where the characteristic exponent is determined by non-isothermal methods. Good agreement with the isothermally determined values was reported for Pd–Be [97] and Pd–B [98], where a combination of eqns. (31) and (33) was used, and for Fe$_{75}$B$_{25}$, where a detailed evaluation of the full $da/dt$ curve was utilized [27].

This section is concluded by mentioning an interesting piece of evidence on the fundamental problem of non-isothermal evaluation. The basic assumption of the usual formalism (which in our case is a direct consequence of the well established theory of nucleation and growth controlled transformations) is that the rate equation is of the same form for both isothermal and non-isothermal measurements. It was actually tested for (GeSe)$_{60}$ (GeTe)$_{40}$ glasses with eqn. (40) and the two sets of measurements were found to merge into a common plot [101]. This result is direct experimental proof of the validity of the isokinetic hypothesis and shows that the alternative formalism, where the rate equation is modified under non-isothermal conditions, is inapplicable.

CONCLUSION

A progress report has been given on the investigation of crystallization in the solid state. It was concluded that a non-isothermal generalization of the laws describing nucleation and growth controlled transformations is only possible along the lines of the isokinetic hypothesis. The alternative formalism, where the transformed fraction is invariant and the rate equation is modified under non-isothermal conditions, is in contradiction with both the general theory and the experiments.

Different methods were reviewed for the isothermal and non-isothermal determination of the kinetic parameters. It was established that the usual precision makes the simultaneous determination of all kinetic parameters from a single non-isothermal experiment very problematic. In addition to methods that are capable of determining $nE$ only, special attention was paid
to the determination of $E$ using temperature shift methods. For a linear heating experiment the transformed fraction at the maximum rate is always $\alpha_m = 1 - 1/e = 0.63$, and is independent of any experimental parameter. The Ozawa and Kissinger methods are thus equivalent and both are generally valid if otherwise identical samples are heated at different rates in their transformation region. In addition to the different quenching rates, the different heating rates in the nucleation region may also result in systematically different samples and then an appropriate correction is necessary.

Experimental results for oxide, chalcogenide and metallic glasses clearly illustrate that identical kinetic parameters can be determined from both isothermal and dynamic experiments in many instances.

ACKNOWLEDGEMENTS

Fruitful discussions with Drs. B. Fogarassy and R. Schiller are gratefully acknowledged.

APPENDIX: EFFECT OF EXPERIMENTAL THERMAL LAG ON MAXIMUM RATE METHODS

As the temperature at which the transformation rate is maximal is usually determined by thermal methods, the reliability of this determination was seriously questioned [102] owing to the finite thermal inertia of any measuring system. While it was shown in some recent publications [103–105] that this negative conclusion is exaggerated, the actual calculation is given here to show the real figures.

If we assume the basic DTA equation in the simplified form:

$$\dot{\alpha} = -\Delta TK/\Delta H - \dot{\Delta} TC_p/\Delta H$$

(neglecting terms arising from experimentally unbalanced conditions for non-stationary calorimetry in the twin arrangement), then $\Delta T$ can be routinely expanded into a Taylor series around $T_0$ where $\Delta T$ is maximal:

$$\Delta T = \Delta T_0 + \left. \frac{d\Delta T}{dT} \right|_{T=T_0} (T - T_0) + \frac{d^2\Delta T}{dT^2} \left. \frac{(T - T_0)^2}{2} \right|_{T=T_0} + \ldots$$

As $\Delta T$ is maximal at $T_0$,

$$\left. \frac{d\Delta T}{dT} \right|_{T=T_0} = 0$$

Introducing the notation

$$D_2 = \left. \frac{d^2\Delta T}{dT^2} \right|_{T=T_0}$$

$$\Delta T = (T - T_0) D_2 \beta$$

$$\dot{\Delta} T = D_2 \beta^2$$
the temperature of the maximum transformation rate is determined by

\[ \Delta H^\ddagger = 0 = \left( -K \Delta T - C_p \Delta T \right) \bigg|_{T=T_m} = -K(T_m - T_0)D T \beta - C_p D T \beta^2 \]

yielding \( T_m = T_0 - C_p \beta / K \).

When the activation energy is determined by plotting \( \ln \beta \) vs. \( 1/T_m \), then

\[ 1/T_m = (1/T_0) / (1 - C_p \beta / T_0 K) \approx 1/T_0 (1 + C_p \beta / T_0 K) \]

Parameters typical of, e.g., the Perkin-Elmer DSC-2 are 5 mg Fe_{75}B_{25} \((C_p = 2.5 \text{ mJ K}^{-1})\), \( T_0 = 700 \text{ K} \), \( K = 10 \text{ mJ K}^{-1} \text{ s}^{-1} \), \( \beta = 0.15 \text{ K s}^{-1} \), thus \( C_p \beta / T_0 K = 5 \times 10^{-5} \), which is negligible. Even in typical macro-DTA with a 300 mg sample and \( K = 20-50 \text{ mJ K}^{-1} \text{ s}^{-1} \) the order of magnitude of the correction never exceeds \( 10^{-3} \), which is still negligible.

REFERENCES

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**Application of fractals in condensed-state processes**

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**Abstract:** Heterogeneous condensed-state processes take place at interfaces of different phases. In general, the surfaces are not perfectly flat and their properties are not homogeneous. They are mostly rough with many irregularities and inhomogeneities. Surface geometrical inhomogeneity is reflected in its chemical inhomogeneity. For the description of the structure of physical objects with inhomogeneous properties (roughness, mass density, heat density, etc.), the methods of fractal geometry can be applied [1]. In this paper, two phenomena will be analyzed, i.e. the heat capacity of fractal structures and the nucleation-induced crystallization.

**Keywords:** fractal geometry, heat capacity, nucleation-induced crystallization

1. Introduction

Heterogeneous condensed-state processes take place at interfaces of different phases. In general, the surfaces are not perfectly flat and their properties are not homogeneous. They are mostly rough with many irregularities and inhomogeneities. Surface geometrical inhomogeneity is reflected in its chemical inhomogeneity. For the description of the structure of physical objects with inhomogeneous properties (roughness, mass density, heat density, etc.), the methods of fractal geometry can be applied [1]. The word „fractal“ originates from the Latin word „fractus“, meaning broken. It is indicated that fractals are widespread and that the fractal geometry is the geometry of Nature [2]. Classical geometry provides a first approximation to the structure of physical objects; it is the language that we use to communicate the designs of technological products and, very approximately, the forms of natural creations. Fractal geometry is an extension of classical geometry. It can be used to make precise models of physical structures of rough surfaces, disordered layers on surfaces and porous objects (such as heterogeneous catalysts). Furthermore, gels, soot and smoke, and most macromolecules are also fractals [3].

Father of the fractal geometry is Benoît Mandelbrot [4]. He described geometric fractals as "a rough or fragmented geometric shape that can be split into parts, each of which is (at least approximately) a reduced-size copy of the whole". Fractals are self-similar objects that exhibit dilatational symmetry. Fractals have details on all scales; therefore Euclidean geometry and classical calculus are insufficient for their description and the fractal geometry is required. Fractals are disordered systems; the disorder is described by generally non-integer dimensions [3]. As long as surface irregularities show scale invariance - that is, dilatational symmetry - they can be characterized by a single number, the fractal dimension. This means that the surface exhibits self-similarity over certain length scales. In other words, the structure exhibited at the
scale of the basic building blocks is reproduced at the level of larger and larger conglomerates. Note that self-similarity implies that the features of a structure look alike at different scales of length or time. This self-similarity of a process at different scales of time can be characterized with a fractal dimension: A higher value of the fractal dimension indicates a higher level of heterogeneity or state of disorder.

Fractals possess non-trivial geometrical properties; in other words, they are geometrical structures with non-integer dimensions. A consequence of the fractal nature is a power-law dependence of a correlation function (rate constant, number of entities) on a coordinate (for example, time or scale). The repeating shape or form does not have to be identical [3]. In this chapter, two illustrative examples of application of the fractal geometry on condensed-state problems are demonstrated.

2. Heat capacity of fractal structures

Within the fractal theory, the number of objects, \( N(r) \), in the circumscribed area with the radius \( r \) can be given as

\[
N(r) = K r^D
\]

where \( K \) is the fractal measure and \( D \) stands for the fractal dimension.

Applying the equipartition theorem [5] heat capacity \( C \) of a solid mass fractal structure embedded in \( E \)-dimensional Euclidean space can be expressed as

\[
C(r) = \frac{dU}{dT} = E k_B N(r) = E k_B K r^D
\]

Here, \( U \) is the internal energy and \( T \) is temperature. In Eq. (2) it is taken into account that each object in the \( E \)-dimensional solid matrix possesses \( E \) vibrational degrees of freedom.

Heat capacity of solids is mostly normalized as

\[
C_v = \frac{1}{m} \frac{dU}{dT}
\]

where \( m \) is the sample mass. If the fractal structure is composed of \( N_m(r) \) objects (atoms) with the average atomic mass \( u \), the sample mass can be expressed as

\[
m(r) = u N_m(r) = u K_m r^{D_m}
\]

where \( K \) means the fractal measure of the mass distribution in the solid with fractal structure and \( D_m \) is the fractal dimension characterizing the mass distribution.

Combining Eqs. (2) - (4), one can get

\[
C_v = \frac{E k_B}{u K_m} r^{D - D_m}
\]

When multiplying both the numerator and denominator of Eq.(5) with the Avogadro constant, we obtain

\[
C_v = \frac{n E R K}{M K_m} r^{D - D_m}
\]

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where $R$ is the gas constant, $M$ is the molar mass of the solid under consideration and $n$ is the number of atoms in a molecule.

It has been derived that the distribution of temperature in the fractal structure embedded in $E$-dimensional space is given as [6-8]

$$T(r) = \frac{K\hbar}{k_B} \frac{\mu^{D-E+2}}{D(D-E+2)}$$ (7)

where $\hbar = h/(2\pi)$ Combination of Eqs. (6) and (7) yields:

$$C_V = \frac{nERK}{MK_m^2} \left[ \frac{RT}{KN_A\hbar} \frac{D(D-E+2)^{D-D_E}}{D-E+2} \right]^D$$ (8)

where $N_A$ is the Avogadro constant. The continuous fractal structure has the fractal dimension between 1 and 3 and is embedded in three-dimensional space ($E=3$). Taking this into account, Eq.(8) can be simplified as:

$$C_V = \frac{3nRK}{MK_m^2} \left[ \frac{RT}{KN_A\hbar} \frac{D(D-1)^{D-D_E}}{D-1} \right]^D$$ (9)

Under the assumption that the distribution of internal energy and the distribution of mass have the same fractal dimension ($D=D_m$), Eq.(9) takes the form

$$C_V = \frac{3nRK}{MK_m^2}$$ (10)

If the distribution of internal energy and the one of mass are identical ($D=D_m$ and $K=K_m$), Eq.(11) reduces to the form expected from the equipartition theorem for high temperatures:

$$C_V = \frac{3nR}{M}$$ (11)

However, the condition of identical distributions of the internal energy and the mass may not necessarily be always fulfilled.

The dependence of heat capacity of fractal objects on temperature, given by Eq.(11), differs from the dependences derived by Einstein or Debye. The Einstein model was derived under the assumption that each atom in a perfect crystal oscillates around its equilibrium position with a single frequency. Debye amended the model taking into account that the atoms in fact oscillate over a range of frequencies from zero up to a maximum value [5]. When deriving Eq. (9), fractal structure of the sample instead of perfectly regular crystalline matrix has been assumed.

3. Nucleation-induced crystallization

Kinetics of condensed-phase processes is very often described by the generalized kinetic equation

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$ (12)
where \( t \) is time and \( \alpha \) is the degree of conversion (or simply conversion). The functions \( k(T) \) and \( f(\alpha) \) are the temperature and conversion functions and should be separable [9-11]. This paragraph deals with the temperature and conversion functions in the process of nucleation-induced crystallization and represents a modification of the approach used by Ozao and Ochiai [12].

The basic concept of the kinetics of nucleation-induced crystallization processes was established by Avrami [13-15]. His model takes into account the interconnection of the growing grains. The assumptions adopted are: (i) Nucleation occurs randomly and homogeneously over the entire untransformed portion of the material; (ii) The growth rate does not depend on the extent of transformation. (iii) Growth occurs at the same rate in all directions. Hence, the constant rate of nucleation can be expressed as

\[
\frac{dn}{dt} = k_n
\]

where \( n \) stands for the number of grains. Volume of one grain with the fractal structure, \( V_1 \), is

\[
V_1 = Kr^D = K(v_1t)^D
\]

Here, \( K \) is the volume conversion factor, \( r \) is the (effective) radius of the grains and \( v_1 \) is the growth rate of grains. First, the growth of grains without their interconnection will be considered. Volume of the transformed matter, \( V \), can be obtained as

\[
V = \int_0^t \frac{dn}{dt} dt = \int_0^t k_n K v_1^D t^D dt = \frac{k_n K v_1^D}{D+1} t^{D+1}
\]

The degree of conversion is defined as the ratio of the volume transformed to the total volume, \( V_o \). From Eq. (15) then follows:

\[
\alpha_w = \frac{k_n K v_1^D}{V_o (D+1)} t^{D+1}
\]

From Eq. (16) one can get

\[
t = \left( \frac{V_o (D+1)}{k_n K v_1^D} \right)^{\frac{1}{D+1}} \alpha_w^{\frac{1}{D+1}}
\]

Differentiation of Eq.(16) gives

\[
\frac{d\alpha_w}{dt} = \frac{k_n K v_1^D}{V_o} t^D
\]

Combination of Eqs. (17) and (18) leads to the result

\[
\frac{d\alpha_w}{dt} = \left( \frac{k_n K v_1^D}{V_o (D+1)} \right)^{\frac{1}{D+1}} \alpha_w^{\frac{1}{D+1}}
\]

If the grains grow sufficiently large as to interconnect one another, only a fraction of \( \alpha_w \) is real; some portion of it lies on previously transformed material and is virtual. Since nucleation
occurs at random, the fraction of overlapped volume should be proportional to the untransformed volume fraction \(1 - \alpha\). Hence, the actual degree of conversion, \(\alpha\), is related to \(\alpha_w\) by the relationship [12-16]

\[
d\alpha = (1 - \alpha)\, d\alpha_w
\]  

(20)

After separation of variables and integration, from Eq. (20) it can be obtained:

\[
\alpha_w = -\ln(1 - \alpha)
\]  

(21)

From Eq. (21) further follows:

\[
\frac{d\alpha}{dt} = (1 - \alpha)\, \frac{d\alpha_w}{dt}
\]  

(22)

Combining Eqs. (19), (21) and (22), one gets

\[
\frac{d\alpha}{dt} = \left(\frac{k_n K_1^0}{V_o} (D+1)^D\right)^{\frac{1}{D+1}} (1 - \alpha)^{\frac{D}{D+1}} [-\ln(1 - \alpha)]^{\frac{D}{D+1}}
\]  

(23)

The fractal dimension of the grains can be \(1 \leq D \leq 3\).

Comparing Eqs. (12) and (23), it is obvious that the temperature function is a composite of several quantities:

\[
k(T) = \left(\frac{k_n K_1^0}{V_o} (D+1)^D\right)^{\frac{1}{D+1}}
\]  

(24)

The conversion function is

\[
f(\alpha) = (1 - \alpha)^{\frac{D}{D+1}} [-\ln(1 - \alpha)]^{\frac{D}{D+1}}
\]  

(25)

Integration of Eq.(23) for a constant temperature leads to an Avrami-like equation:

\[
\alpha = 1 - \exp \left( -\left(\frac{kt}{D+1}\right)^{\frac{D}{D+1}} \right)
\]  

(26)

Main difference with the Avrami derivation is that it is assumed here that the growth of grains may cease at any moment in any direction, not only by impinging on another growing grain. In this way the formation of grains with fractal geometry from the very first moment of crystallization is admitted, not just the formation of spherical particles.

When deriving Eq.(23), it was implicitly assumed that the process was isothermal. For non-isothermal processes, \(k_n\) and \(v_n\) obviously depend on temperature [17]. The dependence of \(k(T)\) on temperature is almost exclusively approximated by the Arrhenius function. In the case of crystal growth, it would be perhaps advisable to employ the equation by Harecourt and Esson [18]

\[
k(T) = AT^m
\]  

(27)

where \(A\) and \(m\) are kinetic parameters. The form of temperature power exponent in Eq.(27) indicates that the fractal nature of matter is taken into account.
4. Conclusions

The two case studies shown above are just illustration of the application of fractal geometry. This chapter has no aspiration to present a complete picture on the subject. For example, Google provides 99900 responses to the keywords „fractal heat capacity“ and 167000 responses to the keywords „fractal crystallization“. Brownian motion has also the fractal character [19]. Applications of fractals for the problems of adsorption, permeability, aggregation and growth, diffusion and reactions, spectroscopy, chemical degradation and other topics are summarized in the monography by Rotschild [20]. Fractal Approach to Heterogeneous Chemistry is reviewed in [21].

However, a reaction medium does not have to be a geometrical fractal in order to exhibit fractal kinetics [22]. Classical reaction kinetics has been found unsatisfactory when the reactants are spatially constrained on the microscopic level by either walls, phase boundaries or force fields. Among the examples of fractal-like kinetics are chemical reactions in the pores of membranes, charge recombination in the colloids and clouds, reactions catalyzed by catalytic islands on noncatalytic supports, etc. When applying classical reaction kinetics to the processes mentioned, anomalously large values of the reaction order can be found (from 3 to 75). The rate constant may depend on time, where the dependence is power-law one [22].

This contribution is a shortened version of chapter 12 from the book „Thermal analysis of micro-, nano- and non-crystalline materials“, edited by. J. Šesták and P. Šimon [23]. The book will appear this year.

References


