

## CRYSTALLIZATION KINETICS ACCOUNTABILITY AND THE CORRESPONDINGLY DEVELOPED GLASS-FORMING CRITERIA – A PERSONAL RECOLLECTION AT THE FORTY YEARS ANNIVERSARIES

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*(Received 12 June 2011; accepted 13 July 2011)*

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### Abstract

*The meaning of experimentally determined characteristic temperatures is analysed in terms of Hruby glass forming criterion. Despite various analysed modifications it reveals that the sensitivity of original criterion is unsurpassable. The applicability of Sestak-Berggren empirical equation for the description of crystallisation kinetics is comparable with the classical modelling based on Johnson-Mehl-Avrami equation. Their employment is certainly dependent to the purpose of evaluation showing their substitution ability and limits.*

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### 1. Introduction

There are numerous important personalities who paved the scientific road toward a better understanding of new phase formation, which is the core of most crystallization processes. It became especially important during the application of fast temperature changes often

leading to the formation of quenched-constrained metastable phases (metallurgy); in extreme providing the unusual *freeze-in state of glasses*. Associated processes remained in the center of research until today, but rich figures have got lost in the extended past of extensive scientific research. Some important scientist are shown in the raw of

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photos below, just to keep in mind illustrious history of exploration of solid-state reactions emphasizing their great protagonists, see Fig. 1., read from the left.



Fig 1. **Gustav H.J. Tammann** (1861-1938) called earliest attention to a tendency, which revealed observation that the higher the melt viscosity at the melting temperature, the lower is its crystallizability [1]. He also invented the term „thermal analysis“ [2]. **Frederik F.H. Zachariasen** (1906-1979) considered the principles how the bonding requirements are met and the nearest neighbor coordination maintained without imposing an exact long range order [3]. **Walter Kauzmann** (1916-2009) analyzed the behavior of liquids at lower temperatures, pointing out that the entropy of undercooled liquid decreases rapidly on cooling towards the kinetic glass transition temperature [4] and extrapolates to the entropy of the crystal at so called Kauzmann temperature. **Jakov I. Frenkel** (1894-1952), became famous for his fundamental book [5] factually introducing the concept of disorder. **David Turnbull** (1915-2007) brilliant material scientists who in 1946 joined the famous General Electric laboratory performing research into nucleation of structural transformations [6], introducing reduced temperatures and demonstrating that such complex glass-forming processes could be quantitatively better understood [7]. Below row, **Robert F. Mehl** (1898-1976) was famous with the American Institute of Mining and Metallurgical concerned with areas of solid-state reactions, diffusion, precipitation, plastic deformation, preferred orientations, and oxidation. He separated the role of nucleation from that of growth of new phases in solid-state transformations and developed generalized theories applicable to re-crystallization describing the volume fraction of a solid transformed in terms of the formation rate and spatial distribution of nuclei and the subsequent growth of the nuclei [8]. **Arnošt Hrubý** (1919-) was an accomplished technologist who synthesized and analyzed thousands of chalcogenide compounds and glasses identifying and describing their properties and proposing so called Hruby glass forming criterion [9]. **Donald R. Uhlmann** (1936-) former director of the Arizona Research Laboratory, fellow and awardee of the American Ceramic Society, the coauthor of both the recognized nucleation-growth theory [10] and the famous Kingery's and Kreidl's fundamental book on ceramics [11]. **Michael C. Weinberg** (1942-2003), architect of various alternative theories on nucleation and glass-formation, [12,13]. **Edgard D. Zanotto** (1954-) another representative of emerging generation of new theoretical kineticists responsible for the advanced nucleation and crystallization theories mostly applied to silicate glasses [14,15], the chair of the ICG (TC7) committee on glass crystallization and the editor of *J Non-cryst. Sol.*

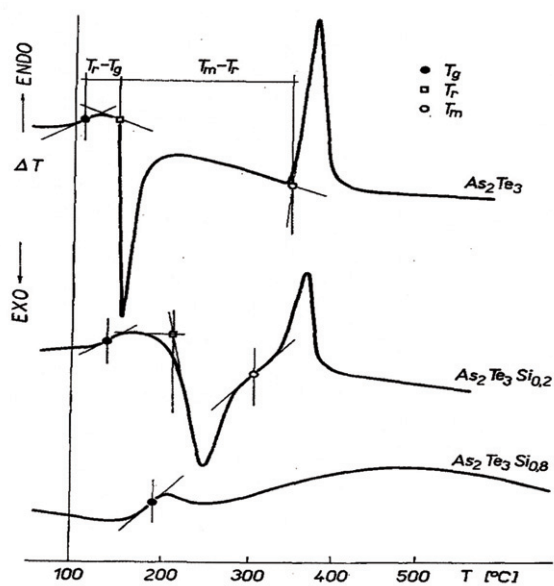
A special attention should be paid to the Institute of Physics of the former Czechoslovak Academy of Sciences, which in the turn of 1970's was one of the leading institutions in solid state physics and chemistry [16-19] within the so called Eastern socialist block then dominated by the former Soviet Union. Its employee *Arnošt Hrubý* [9] was a gifted technologist who investigating thermal behaviors of chalcogenides mainly by means of DTA. His famous glass-forming criterion published in a less known Czech Journal of Physics [9] nevertheless received abundant citations responses [19]. His coworker J. Šesták contributed kinetic study of crystallization processes by various means of thermal analysis [16,17] showing the way how to formulate a generalized model of logistic (autocatalytic) equation [18] effectively analogous to nucleation-growth kinetics. All these topics got a prospect to be extensively cited in the literature, for example, *Hrubý* [9] gained as many as 372 and *Sestak Berggren* equation [18,19] 566 responses becoming thus the best cited papers in the respective journal [19], which are comparable with the Jander equation on diffusion [20] with 551 citations. It is still below *Mehl* paper [8] on general kinetics of phase changes with 2172 or *Kissinger* paper [21] on DTA determined kinetics with 4461 but analogous to similar *Uhlmann* paper [10] on crystallization kinetic 417 or *Zanotto* paper [14] on generalized nucleation theory with 190 citations. The soaring output of the kinetic papers published during 1970s is thus worth of attention revising their meaning and uncovering some generalized correlations between the easiness of crystallization and

its opposite hindrance, i.e., contradictory obstruction of glass-forming ability and associated glass stability. The classical nucleation-growth description became thus important and is analyzed in terms of the Šesták-Berggren empirical equation [18] all hints instigated at the occasion of the forty years anniversary of the earliest papers publication [9,18].

### **Hruby glass-forming coefficient and related criteria**

*Disordered matter* still presents stringent conceptual difficulties being prepared under extreme conditions of either the self-cooling of compositionally adjusted mixtures [22] (silicates, alloys even in metallurgy) or by attuned quenching [23] (usually applied to the ribbon preparation of metallic glasses). Coupled and repeatedly confusing concepts of *amorphous and glassy states* were re-examined recently by *Queiroz and Šesták* [24-26] considering thermodynamic aspects of glasses in the glass transition region. Associated parameters endeavoring the prediction the *glass forming ability* (GFA) and/or the consequent *glass stability* (GS) of the constrained states of freeze-in glasses are of substantial terminology meaning [22,26]. It is often related to the *time-temperature-transformation* (T-T-T) diagram [22] common for the description of material annealing creditable for the subsequent occurrence of nucleation-growth kinetics. However, T-T-T is rarely available and moreover needs to be predicted on the assumption of homogeneous nucleation, which is an unlikely event in practice. When a glassy matter does happen to be

experimentally accessible upon a suitable melt quenching (*critical cooling rate,  $R_c$* ) down from its *melting point ( $T_m$ )* through the *glass transition region (GTR)*, defined by the *mean glass transition temperature ( $T_g$ )* certain data became accessible for such a material identification [27-33]. Consequently a range of following criteria was proposed.



**Fig. 2.** Original proposal of reading the characteristic temperatures in the Hruby glass-forming criterion

A rather sensitive interrelation to the *glass formation (GF)* particularity can be found on basis of the widespread *Hruby parameter* [9,31]. It is typically available upon a physical preparation of a given type of glass and can be calculated as  $K_H = (T_c - T_g)/(T_m - T_c)$  on basis of experimentally detectable quantizes (usually figured out by DTA [9, 31, 32], such as  $T_c$ , which is the *onset of crystallization temperature*). A more receptive parameter toward the glass

formation was assumed by *Saad and Poulain* [34] which took into their consideration the *width of a DTA/DSC peak*, i.e., the difference between the onset of crystallization  $T_c$  and its maximal value  $T_x$  [34, 35]. Such a new criterion  $(T_x - T_c) \cdot (T_c - T_g) / T_g$  comprises the unit of Kelvin, but is capable to become dimensionless if weighted by squared  $T_g$ . The other popular glass-forming parameters was proposed by *Weinberg* [36]  $K_W = (T_c - T_g)/T_m$  and in the recent years, various other parameters have been investigated, such as the parameter envisaged by *Lu and Liu* [37, 38] as  $K_{LL} = T_c / (T_g + T_m)$ . There are additional parameters proposed in the papers [39-42] mostly related to the previously mentioned characteristic temperatures dealt in details with allied papers [31-57].

In the paper by *Weinberg* [43] the trends in GFA and GS were compared with systematic changes in the melting entropy,  $\Delta S_m$  and the viscosity  $\eta$  concluding that GFA and GS (defined by  $(T_c - T_g)/T_m$ ) are poorly related. *Weinberg* [36] also derived the time necessary to crystallize a minimum detectable fraction based again on a classical homogeneous nucleation and screw dislocation growth in stoichiometric glasses. *Time criteria* were used to assess GFA and test the reliability of two particular GS parameters (given by the previously mentioned expressions [34, 43]) observing that the stability of glasses with the parallel viscosity curves  $\eta(T)$  could be qualitatively weighed up. *Zanotto et al* [44] used experimental values and found a correlation between the *Hruby parameter* [9] of GS and GFA being, however, contradictory in relation to the theoretical calculations of *Weinberg*. *Avramov et al.* [45] extended the

calculations of *Weinberg* [43] but tested a different assumption, which is supported by experimental data demonstrating that GFA and GS follow the same trend and are jointly interrelated. Recently, several other important studies have appeared [46-55], which demonstrate correlation between the GS parameters and critical cooling rate  $R_c$ , or between the GS parameters and the maximum sample thickness, i.e. the section diameter  $D_{max}$ , by which the glass forming ability are estimated [37, 39-42, 46, 47]. It again reveals a rather good correlation between GFA and GS, based on the above three characteristics given by the Hrubý ( $K_H$ ), Weinberg ( $K_W$ ) and Lu-Liu ( $K_{LL}$ ). *Zanotto et al* [46] proved that for the oxide glasses a very good correlation between the Hrubý parameter and GFA can exist and another good correlation between  $K_{LL}$  and GFA was also established [46, 49]. Another exploit was found even for metallic glasses [50, 51].

The work of *Zanotto et al* [46] proves that  $T_{rg}$  has the weaker correlation with GFA for oxide glasses than  $K_H$ ,  $K_W$  and  $K_{LL}$ . Similarly, Lu and Liu showed that  $T_{rg}$  has the weaker correlation with GFA than their parameter  $K_{LL}$  for glasses analyzed in [37]. Larger values of the coefficients  $K_H$ ,  $K_W$  and  $K_{LL}$  imply higher stability of the glass in respect to devitrification [45]. Also, when comparing one glass to another, it is essential to know how large the relative change of the given parameter is and how it can be compared with the relative change of other GS parameters. In other words, it is necessary to know which of the GS parameters shows the fastest change.

*Kozmidis-Petrovic* [52] pointed the fact

that all the coefficients  $K_H$ ,  $K_W$  and  $K_{LL}$ , include the identical three characteristic temperatures possible to express them in a somewhat distinctive way by mere ratios of respective temperatures, such as  $m = T_m/T_g$  and  $r = T_c/T_g$ , where that the following relations always sustain, i.e. :  $m > 1$ ,  $r \geq 1$ ,  $m > r$ . Thus the both  $K_H$  and  $K_{LL}$  is possible to incept the crystallization temperature  $T_x$  with the maximum crystallization peak temperature  $T_c$  as was shown by *Zanotto et al* [46]. After simple mathematical transformations we obtain  $K_H = (r-1)/(m-r)$ ,  $K_W = (r-1)/m$  and  $K_{LL} = r/(m+1)$ . Using the substituted  $r$  and  $m$ , the GS parameters can be expressed indirectly via the reduced glass transition temperature  $T_{rg}$  and super cooled region  $\Delta T_{xg}$ . It is because the parameter  $m$  represents the reciprocal value of  $T_{rg}$ , and the parameter  $r$  can be correlated to  $\Delta T_{xg}$ , as was shown in the work of *Lu and Liu* [37] and *Mondal* [53] or in a recent work by *Zhang et al* [54]. In order to enable the comparison for different glasses [55], the value of the super cooled region is divided by  $T_g$  [37], which gives  $(T_c - T_g)/T_g = r - 1$ . *Mondal et al* [53] used the same normalization and proposed that  $T_x/T_g (= r)$  can also be considered as a measure of the *thermal stability* of glass. *Zhang et al* [54] introduced the factor of *crystallization resistance*  $T_g/(2T_x - T_g)$  ( $= 1/(2r - 1)$ ).

In order to derive expressions for the coefficients relative changes, *Kozmidis-Petrovic* [31, 52, 57] first took logarithms of  $K_H$ ,  $K_W$  and  $K_{LL}$  and then differentiated the obtained values achieving inequality  $dK_H/K_H > dK_W/K_W > dK_{LL}/K_{LL}$ , which is valid when  $d(T_c/T_g) > d(T_m/T_g)$  i.e. if the condition  $dr > dm$  is satisfied. Resulting

relative changes of the GS parameters will also hold under a less stringent condition  $dr/r > dm/m$ . The relative change of  $K_{LL}$  will always have the smallest value being never greater than the relative change of the original Hrubý parameter [9, 31, 57], which satisfactorily the *best sensitivity*  $K_H$ . The ensuing relation between the maximal values of relative changes of the individual K-parameters approves thus the priority of Hrubý coefficient [4,57] by  $(dK_H/K_H)_{max} > (dK_W/K_W)_{max} > (dK_{LL}/K_{LL})_{max}$

### Šesták-Berggren (SB) kinetic equation for a generalized crystallization

At the anniversary [19] of Šesták-Berggren (S-B) equation [18], it reads as  $d\alpha/dt \cong \alpha^m(1-\alpha)^n$ , (where  $\alpha$  is the dimensionless degree of crystallization,  $t$  is time,  $d\alpha/dt$  is the crystallization rate and the omitted proportional Arrhenius constant  $\exp(-E/RT)$  incorporates temperature,  $T$ ). S-B was proposed in a particular association with a well established kinetic model introduced jointly by Johnson-Mehl-Avrami (JMA) [8, 18, 58-62] as  $d\alpha/dt \cong \{-\ln(1-\alpha)\}^p(1-\alpha)$ . Since 1971, S-B received abundant citation responses and even became a part in the titles of various kinetic papers [62-66]. It is worth noting that upon the Taylor's expansion the function  $\{-\ln(1-\alpha)\}^p$  can display a certain mathematical inter-convertibility upon the expansion and recombination to the matching  $\alpha^m$  [58-61]).

The two appropriately paired exponents of the S-B equation ( $m$  and  $n$ ) are suitable for a wide-ranging kinetic assessment, which includes the classical model of autocatalytic reaction (where  $m=1$  and  $n=1$ ) often called

*Prout-Tompkin* equation (turning thus into its limiting case [61]). The increasing value of  $m$  often indicates a more important role of the precipitated phase on the overall kinetics consequently showing that this two parameter model preserve its physical meaning for  $m \leq 1$  [61, 62]. It also appears that a higher value of the second kinetic exponent ( $n > 1$ ) signifies increasing reaction complexity. Besides the S-B equation subsists as a generalized operate based on the *logistic function* [59, 61], a  $\{\alpha(1-\alpha)\}$ , which is customarily exploited to depict the case of population growth where  $a$  is the proportional factor of so called 'attractivity'. It consists of two essential but counteracting parts, the first one responsible for *mortality*  $\cong \alpha^m$  (i.e., reactant disappearance and the product formation) and the other for *fertility*  $\cong (1-\alpha)^n$  (i.e., a kind of products' hindrance generally accepted as an counter-parting 'autocatalytic' effect [61]). The non-integral exponents,  $m$  and  $n$ , play thus the similar role as a broadly assumed non-integral dimensions common in the natural *world of fractals* [62].

The S-B equation can be found credulous for serviceability as an alternative to the classical JMA equation [61-66] and thus exploitable for an assortment of model descriptions of both the interface-controlled and the diffusion-limited crystallization. Such a modeling starts from an original comprehensive form of  $\ln(1-\alpha) = -k_T t^r$ , where the general exponent,  $r$ , can be seen as a multipart number of a robust (so called overall) analysis. In terms of DTA measurements it reveals that the overall apparent values of activation energies  $E_{app}$  [67] can be commonly correlated to the

partial activation energies of nucleation,  $E_N$ , growth,  $E_G$  and/or diffusion,  $E_D$  by a simple relation  $E_{app} = (aE_N + bE_G)/(a + b)$  where  $a$  and  $b$  are characteristic multiplying constants providing that the denominator ( $a + b$ ) equals to the power exponent,  $r$ , of the original JMA equation, and the value  $b$  corresponds to 1 or  $\frac{1}{2}$  related to the movement of growth front controlled by either chemical reaction (1) or diffusion ( $\frac{1}{2}$ ) [16, 61, 67]. Moreover, the coefficients  $d$  and  $b$  are associated with the nucleation velocity and the growth dimension, respectively. However, it endowed with a rather complex pattern so far mathematically soluble but experimentally problematic in order to reach reliable association with (desirable) microscopic observations [58].

In 1990 this S-B equation was completed [68] by the conjecture of the so called *accommodation function*,  $h(\alpha)$  which is a effortless empirical function containing the smallest possible number of constant and enabling certain flexibility in order to sufficiently match mathematically the real course of a process under study. In such case, the kinetic model of a heterogeneous reaction is factually assumed to be a *distorted* case of a simpler (ideal) instance of homogeneous kinetic prototype, i.e.,  $h(\alpha)f(\alpha) \approx h(\alpha)(1-\alpha)^n$  [68]. It thus gives a credit to the recognition of a certain 'defect state' (imperfection, non-ideality, heterogeneity such as the *controlling role of interfaces*). The function  $h(\alpha)$  can be equally  $\alpha^m$  and/or  $[-\ln(1-\alpha)]^p$  displaying in a way, above mentioned inter-convertibility with the JMA model function, which brought to kinetics an additional sphere of a more widespread applicability approaching thus the model-free domain of kinetic evaluations

enabling, however, certain but limited conversion to the traditional geometrical models [60-70]. There is a certain correlation between the S-B exponents  $m$ - $n$  and JMA exponents  $r$  (and  $p$ ) [60, 62, 69, 70] see Fig 3.

Another agreeably workable alternative to the JMA crystallization is the mechanism of so called *normal-grain-growth* (NGG) resembling mode close to the mathematical modeling of phase-boundary reactions [59-61], i.e.,  $\alpha^m(1-\alpha)^n$  where  $m \rightarrow 0$ . This case is abbreviated as the *Atkinson's* NGG model [72], which has been effectively applied by *Illekova* [73, 74]. NGG factually reflects the process of coarsening of the nano-crystalline phase, when grain size falls below 10 nm, which is common in some metastable metallurgical alloys and constrained glasses. In this instance the DSC/DTA exothermic crystallization peaks is converted into different shape possessing atypical symmetry, which is the result of rationale arising from the differences in JMA and NGG mechanisms [72-74].

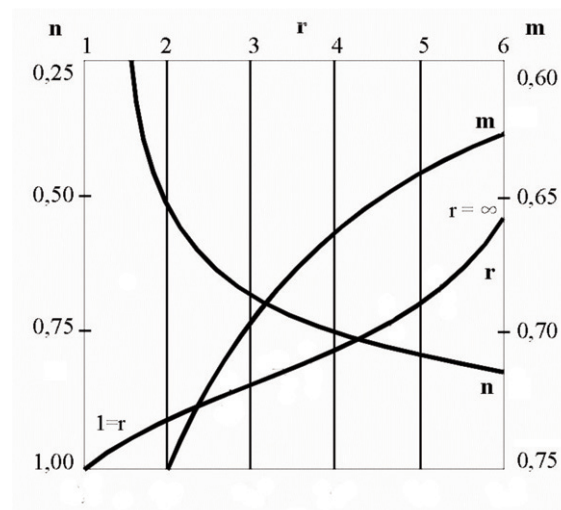


Fig. 3. Portrayal correlation between JMA ( $r$ ) and SB ( $m$ - $n$ ) exponents.

## Conclusions

The determination of characteristic temperatures is an ordinary task in thermal analysis [59-61, 75] (and likewise derived SB-equation) possibly providing a rather good mathematical match toward the trial modeling of crystallization, see Fig.4. It should be reminded that somehow inconsequential information is involved

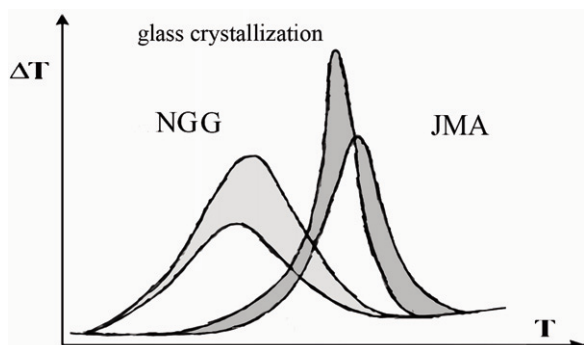


Fig. 4. Illustrative cases of experimental DTA/DSC traces demonstrating possibility of twofold kinetics for an analogous crystallization of two brands of similarly vitrified alloys [74] melt-quenched by a single roll technique to form ribbons (10-20 $\mu\text{m}$  thick and 10mm wide). Right is the tangible glass of composition of  $\text{Fe}_{75}\text{Si}_{15}\text{B}_{10}$  while left is the nano-crystallized finemetal with a comparable stoichiometry  $\text{Fe}_{74}\text{Si}_{13}\text{B}_9\text{Cu}_1\text{Nb}_3$  [80, 81] (just with a small doping of Cu and Nb). Both flat samples were treated correspondingly, freeze-in ribbons were cut in several pieces and pressed into a Pt-cell with the in-weight of 15mg; heating rate was 40 K/min (applied under nitrogen inert atmosphere to avoid oxidation). The ribbons were pre-annealed at the fixed temperature of 500 $^\circ\text{C}$  and annealing time was progressively prolonged, for the sake of simplicity the particular curves fall within the shaded areas.

Right: the classical JMA nucleation-growth mechanism [8, 58-62], which display the non-integral values of S-B exponents [16-18, 70], i.e.,  $m < 1$  and dimension dependent  $1 < n < 3$  (in conjunction with a nucleation short-range diffusion plausibly involving their radii relation  $r/r_0 = (1 - a)^{1/n}$ , where  $r$  and  $r_0$  are the radii at  $t = t$  and  $t = 0$ ). The resulting sharp peak apexes are typically shifted along with the increased heating to commonly follow the kinetic evaluation method by Kissinger [21], widely employed in the literature [59-69].

Left: a more distinctive Atkinson [72-74] normal-grain-growth (NGG) of nano-particles' coarsening, which show signs of phase boundary reactions (controlled by interface propagation). Such a process is reliant on a longer range diffusion and nano-particles' initial and actual size  $r_0$  and  $r$ . For  $m$  approaching zero ( $a^m \sim 1$ ) the scheming exponent  $n$  holds for the reaction rate in the form of  $(1 - a)^{n+1}/(n r_0^n)$ . In consequence the experimentally measured DTA peaks ( $\Delta T$  vs.  $T$ ) reveal different symmetry with an atypical behavior of broadened apexes and their shifting under increased heating rate [74,80], which may cause certain intricacy in traditional kinetic appraisals.

about the actual portrayal of mechanism. If we assume, however, that the goal of most studies is a more and less pragmatic [59-61, 71, 76, 77], i.e., the reportable determination of an unspecific data on reaction mechanism the SB-equation subsist satisfactory. However, if we are seeking a correlation to one of the confidential physical-geometric models we have to look for an alternative representation based on otherwise observable morphology between the true reaction image and the theoretical portrait symbolized by the model assumed. However, a more in-depth seeking may correspond with an innovative so called *model-free kinetics* (e.g. Šimon [78]) and/or *congruent dissociative vaporization kinetics* (e.g. L'vov [79]). In the first case [78] the



kinetic parameters occurring in  $(T - \alpha)$  functions are only perceived quantities (similarly to the widespread portrayal of ‘apparentness’), possessing no traditional ‘mechanistic’ interpretation while the second case [79] provides the temperature coefficient of reaction rate identifiable with the molar enthalpy (van’t Hoff equation) rather than assuming (never justified) participation of an activated intermediate (as in the Arrhenius model).

### Acknowledgement

*The results were developed within the CENTEM project, reg. no. CZ.1.05/2.1.00/03.0088 that is co-funded from the ERDF within the OP RDI program of the Ministry of Education, Youth and Sports“.*

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