J Therm Anal Calorim (2014) 117:3–7
DOI 10.1007/s10973-014-3810-7

Is the original Kissinger equation obsolete today: not obsolete the entire non-isothermal kinetics?

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Received: 18 February 2014 / Accepted: 31 March 2014 / Published online: 27 April 2014

Abstract Physical meaning of activation energy is analyzed from the viewpoint of non-isothermal kinetic evaluation. The term of heat inertia, meaning the degree of slowness with which the temperature of a body approaches that of its surroundings, is examined, and its impact on activation energy determination is discussed, which is particularly functional for a DTA peak kinetic appraisal. Impact of a process equilibrium background on kinetics is recollected as specifically important for Kissinger kinetic evaluation distinguishing competent case of glass cold crystallization on heating but unsuitable for melt crystallization on cooling without introducing additional thermodynamic terms. Parallel to non-Arrhenian kind of kinetics, an analogous model-free description is advocated accentuating a generalized approach by logistic functions.

Keywords Kissinger kinetic evaluation · DTA · Activation energy · Heat inertia · Peak rectification · Crystallization · Equilibrium background · Logistic

In their recent paper [1], Svoboda and Málek criticized the applicability of popular Kissinger equation [2, 3] which is an excellent article but falls to those in which a certain continuity is reflected toward a never ending story how to determine some publishable numerical figures. Regrettably, we are witnessing situation when scientists are too busy with administration having thus not enough time to get familiar with previous views. Let me remind some of its history accentuating my own experience with chasing specifies of activation energy, abbreviated as E. In my first public lecture [4], in the middle of sixties, I already pointed out that the E value may not stay constant when taking into account the mutual interdependence of pre-exponential factor with its exponential term (E), latter called kinetic compensation effect [5, 6]). It has not become fully accepted in the kinetic literature [7] as yet while still deciphering variously shared relations often incorporating changes in the reaction mechanism. Ten years later [8], I noticed that the standing practice of kinetic evaluation of a DTA peak involves certain inadequacy when deriving kinetic parameters [7] because there does not exist a desired match between the maximum values of the temperature difference (DTA peak profile) and of the associated reaction rate. Therefore, an experimental method how to approve such a DTA appraisal by inserting a well-defined Joule process was investigationally introduced [10]. Though the ensuing call for an indispensable rectification of any DTA peak prior its kinetic exploitation was published in a distinguished journal [9], it has stayed away from an appropriate attention until now [11, 12]. It means that there is negligence to neither the change of existing long-lasting practice nor its revolt by impediments toward a readily available kinetic software approving thus an impression that no one ever listens to the other that is understandable in the overwhelming information world which brought instead autonomy: confusion.

Similar philosophy has been persisting in another important but yet overlooked issue, which is the consequence of proximity to equilibrium, i.e., the effect of process equilibrium background [13–15], effecting again the value of resultant E. It is closely linked with the mathematical procedures, namely integration [16] of the basic

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This comment refers to the article available at doi:10.1007/s10973-013-3486-4.

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kinetic equation and a prior determination of the so-called constitutive equation [17]. A number of these kinetic difficulties [18, 19] were thoroughly analyzed [20–23], but thermoanalysts are still holding on their established practices specialized more and less on the numerical accuracy than on the data reliability.

Let us return to the everlasting commentary on the Kissinger evaluation method [1–3]. Its foundation is based on the historical treaty by Murray and White [24], the mathematical background of which was historically analyzed in detail elsewhere [25, 26]. The Kissinger method has received as many as 4,500 citation responses [26] and was revised and modified numerously, noting just this JTAC journal during past thirty years (from [27] to [28]), which received again countless literature quotations [26]. Various adaptations were mostly directed to the availability of various mathematical models of reaction mechanism [29, 30] being concluded that the entire models are not that much responsible to the yielding value of E [31]. No one, however, took attention to the method origin [2, 3] trying to locate where and how this kinetic evaluation was born indicative thus of true conditions for the shift of a DTA peak apex with an increasing heating rate. The original derivation of Kissinger formula [2, 3] did not account on the consequence of heat inertia, which is inherent in the buildup of any DTA peak [10–12]. Triggered disparity between the seeking maximum of reaction rate and the associated upper limit (apex) of a DTA peak prevails over other numerical errors arising from various mathematical adjustments. The implementation of a resourceful view to the DTA theory was thoroughly revealed in detail in our previous papers [11, 12]. It again shows the lack of attention to the area under actual discussion though appearing in our previous papers [9, 32] markedly accepted in other topics of investigation [33–39] being recognized as a general tendency of substances to resist temperature changes (especially acknowledged as a thermocouple thermal inertia effect [33, 34]). For example, thermal inertia has been long purposeful to environmental studies [35, 36], buildings [37], and material science [38]. Various dictionaries counsel the term thermal inertia as a measure of the receptiveness of a material to differences in temperature which can be referred to as a kind of volume-specific heat capacity capable to circumscribe the facility of a given substance to penetratingly accumulate internal energy (physically proportional to a square root of the product of material density, specific heat capacity, and thermal conductivity) [39]. Another definition points on the degree of slowness with which the temperature of a body approaches that of its surroundings.

Thermal inertia was well treated in the paper by Vold [40] (preceding Kissinger [3] by almost ten years) and consequently particularized for kinetics by Blumberg [41]. Ignoring the papers [9–12, 32] and even the books [42–45] where this effect was revealed is a sign of reluctance or better laziness to adapt to new ideas. Moreover, it is not only heat inertia distortion involved in DTA measurements but also there appears another trouble due to the determination of reaction temperature when a gradient distribution exists in the solid sample. Early fifties, it was already noticed by Smyth [46], mathematically specified in [11] and practically elaborated toward a use of averaged temperature in [47].

Certainly, there are more yet undecided particularities in the application of Kissinger method [2, 3, 12, 48, 49] the mathematics of which is valid only for a process transfer from its non-equilibrium state to equilibrium one [15] which is the most common case of glass crystallization. Such a process of ''cold'' crystallization begins immediately as the freeze-in and ready-to-grow nuclei start growing upon heating, because they are already present as a product of the previous process of melt cooling. This, however, is not true for a process of melt crystallization upon cooling where together with the melt undercooling the nuclei are first forced to begin with their formation which occurrence needs a certain nucleation energy (E) to emerge. Such a term will possibly contain some other thermodynamic data as the change of formation enthalpy (f), ΔH_{r}, driving force (undercooling), ΔT_{r}, attuned to the reduced (r) temperatures $T_{\mathrm{r}} = T/T_{\mathrm{o}}$ (most common approximations being $\Delta H_{\mathrm{r}}\ T_{\mathrm{r}}/(\Delta T_{\mathrm{r}})^2$ and/or $\Delta H_{\mathrm{r}}/(\Delta T_{\mathrm{r}}\ T_{\mathrm{r}})^2$) which would become a part of the (apparent) activation energies. Associated mathematical derivation makes, however, the resulting equation rather complicated [48, 49]. Certainly, there is yet another mathematical approach, which can be perceptibly anticipated to all transformation processes following the departure from equilibrium [15] where the classical Kissinger plot cannot be straightforwardly applied [49]. In the case of interaction between kinetics and proximity to equilibrium [13, 18, 19], the meaning of E becomes doubtful [50–54].

A special issue of kinetics encompasses illimitable predicaments associated with a popular subject of exploration focused on finding a suitable representation of reaction mechanism of solid-state processes, where the boundlessly derived mathematical models [55–57] are based on geometrical portrayal of certain theoretical ideas about the reaction pathway. It describes the evolution of degree of reaction within the framework of an identifiable $f(\alpha)$-expression often including non-integral or better fractal exponents [56–59] thus capable to upgrade the impact of reaction non-homogeneity in a relation to classical homogeneous reactions (where $f(\alpha) = (1 - \alpha)^n$ and $n = 1, 2,$ and 3 are the so-called reaction orders as employed in the Kissinger original derivation [3]). Hence, we can speak about distorted

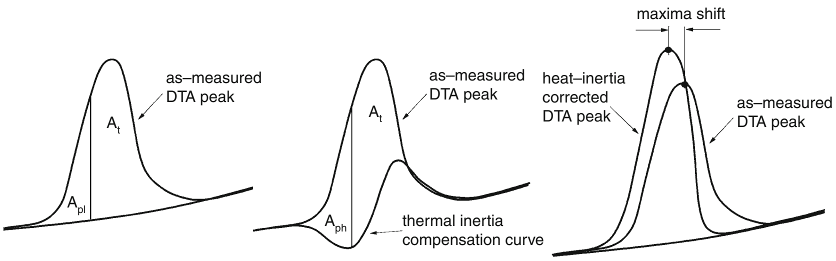

Fig. 1 Gradual refinements applied on an explicatory DTA peak (↑x-axis is the recorded temperature deviation, ΔT, and the →y-axis settles time, t). *Left* linearly interpolated peak background where A_t is the peak total area and A_{pl} is the partitioned area (providing the traditional value of degree of reaction as $\alpha_{pl} \cong A_{pl}/ A_t$). *Middle* incorporation of the heat inertia term ($\approx d\Delta T/dt$) which causes the s-shaping of peak background while the total peak area, A_t, is preserved but altering the partitioned area, A*ph* (changing thus to the factual value of degree of reaction to $\alpha_{ph} \cong A_{ph}/A_t$, because $A_{ph} \neq A_{pl}$). *Right* comparison of the original (as-cased instrumentally) and mathematically rectified (incorporating thermal inertia) peaks (normalized to the same linear background) displaying that both the peak inner areas, A_t, are preserved identical (calorimetry) but changing the shape and position (kinetics) of rectified peak

cases of simpler/ideal models becoming suitable to describe more complex situation of spatial/heterogeneous reactions where a supplementary added function, α^m, can undertake a role of accommodation [60] for variously defect/imperfect states. Inaugurating thus a simple logistic equation $(1 - \alpha)^n \alpha^m$ [31, 59] where the α-term keeps going for the process advancement while the term with $(1 - \alpha)$ accounts the process proceeding only in that reacting part that is not yet transformed. In other words [56], this means mortality (α^m describing reactant disappearance and the product formation) and the complementary fertility [for a reactant still ready to react in response of $(1 - \alpha)^n$]. In this fashion, it bears a logical justification for any process though having no straight correlation to a particular reaction mechanism [54–60] which anyhow is usually off the confirmation by direct complementary observations (microscopy). For a specific case of nucleation-growth models [55–57], α^m stays interchanged by $\{-\ln (1 - \alpha]\}^p$ which, however, sound strange concerning the logic of reaction progress [31]. Nevertheless, it can be opportunely expended to a series then transformable back to a kind of α^m -function. There are attempts to mathematically correlate variously termed equations each other [55], but it seems pointless as the particular models [56, 57] are more and less suited for publication often microscopically uncorrelated. Like the escalation of non-Arrhenian kinetics [61], we can well proceed with an analogous model-free description of the reaction mechanism merely based on logistic functions [31] though being a ''non-prototype'' (purely phenomenological) execution. This idea can be promoted by studying reactions under a rate-controlled mode [62] which can facilitate diminishing undesired temperature gradients [46] (auxiliary distorting the trial for mechanism resolution.)

We should imagine that other alternating physical–chemical approaches [61–65] can be anticipated to be taken operational into our kinetic conservative contemplation. Mathematical custom of a habitual application of an exponential term can be substituted by another premise [7, 61] which, certainly, would require a more patient approach of scientists in reading previous and simultaneous papers on similar, even historically recognized, subjects. We should become ready to question the traditional meaning of E as a broadly expedient quantity [51–53, 63], the determination of which still seems to prevail in evaluations of kinetic behavior of solid-state process [56, 57] presumptuous of the Maxwell–Boltzmann energy distribution applicable as a possible explanation for the Arrhenius-type temperature dependence analogous to the electronic energy distribution at the impurity levels in semiconductor interfaces [7, 57]. In the historical recollection of kinetic papers, many values of so-far published E [48, 49, 63] can stay numerically erroneous but that does not deteriorate the scientific level of reports. However, I am almost convinced that my notification of such widespread inadequacies will not bring applause from the conformist readers because it would factually imply that copious articles [26] concerning E determination would mean the inclusion of incorrect data [49].

In conclusion we can pronounce that the amalgamation of heat inertia effect into our everyday thermal analysis kinetics [9–12, 45] would revolutionize not only its enduring practice [66] but also built-in philosophy [18] changing both the consequence of the of DTA apex disposition [12, 48, 49] and the values of entire degree of reaction customarily derived by the partitioning of DTA peak area, see Fig. 1., early introduces in [25, 26, 67] and widely applied to the kinetic appraisal on almost all DTA figures [21, 42, 44, 45, 55, 57]. To our delight, we found that there appeared a new tentative attempt to put the otherwise assumed hear inertia (as time leg) into the computer evaluation practice [68] - let us follow these motivation examples [9, 68] though having been thirty years apart [9, 68] and comprehending dissimilar approaches.

Acknowledgements 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 inside the OP RDI program of the Ministry of Education, Youth, and Sports. Deep thanks are due to my colleague Pavel Holba who is an inexhaustible source of ideas, wisdom, and companionship.

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