Letter to Editor

DOUBTS ON KISSINGER´S METHOD OF KINETIC EVALUATION BASED ON SEVERAL CONCEPTUAL MODELS SHOWING THE DIFFERENCE BETWEEN THE MAXIMUM OF REACTION RATE AND THE EXTREME OF A DTA PEAK [#]

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Abstract

The famous Kissinger´s kinetic evaluation method (Anal. Chem. 1957) is examined with respect to the feasible impact of the individual quantities and assumptions involved, namely the model of reaction mechanism, $f(\alpha)$ (with the iso- and noniso-thermal degrees of conversion, α and λ) the rate constant, $k(T)$ (and associated activation energy, E), heating/cooling rate, β (supplementing additional thermodynamic term for the melt undercooling, ΔT) and above all, the association of the characteristic temperature, T_m, with the DTA peak apex. It is shown that the Kissinger´s equation, in contrary to the results of Vold (Anal. Chem. 1949), is omitting the term of heat inertia arising from the true balance of heat fluxes. The absence of this term skews the evaluated values of activation energies.

Keywords: Differential thermal analysis (DTA), kinetics, reaction mechanism, Kissinger, heating/cooling, equilibrium background, undercooling, maximum reaction rate, peak apex

1. Introduction – Kissinger´s equation

While studying kinetics of thermal decomposition of clays Murray and White [1] introduced the second derivative of a standard rate equation [2, 3] as early as in 1955

$$r(\alpha,T) = d\alpha/dt = k(T)\, f(\alpha) = A\exp(-B/T)\, f(\alpha) \quad (1)$$

where r, α, t, T, E, A and B ($= E/R$) are reaction rate, degree of conversion, time, temperature, activation energy, pre-exponential factor and a constant (comprising the ratio of activation energy, E, and universal gas constant, R) and providing a widespread form [2, 3]:

$$d(d\alpha/dt)/dt = d\alpha/dt\, [B/T^2_m\, dT/dt + df(\alpha_m)/d\alpha\, A\exp(-B/T_m)] \quad (2)$$

This is equal zero at the moment of maximum reaction rate (m) occurring at a characteristic temperature, T_m. Under a constant heating rate, $\beta = dT/dt$, the eq. (2) can be rewrite as follows

$$(d\alpha/dt)\, [B\beta/T^2_m + df(\alpha_m)/d\alpha\, A\exp(-B/T_m)] = 0 \quad (3)$$

Because the term $(d\alpha/dt)$ is never zero, the expression in square brackets can be adapted

according to

$$[B\beta/T^2_m + df(\alpha_m)/d\alpha\, A\exp(-B/T_m)] = 0 \quad (4)$$

The final form of which equals to a well known equation

$$\beta/T^2_m = -df(\alpha_m)/d\alpha\, (A/B)\exp(-B/T_m) \quad (5)$$

and its logarithmic form encompasses the famous Kissinger´s equation [3,4]

$$\log(\beta/T^2_m) = B/T_m + const \quad (6)$$

Eqs. (5) and/or (6) have undertook various mathematical modifications and applicability upgrading [6-19] in order to improve data logarithmic fitting of individual experimental measurements while endorsing reliability of evaluated activation energies [20] . Kissinger equation [5] received as many as four and half thousand citation responses [21] and its Augis and Bennet variant [8] became one of the best time-honored papers of Journal of Thermal Analysis with four hundred fifty citations [21] . There have been published numerous papers employing this method for experimental data evaluation producing thus plentiful values of activation energies - mostly as a major subject of publication. However, only few

papers analyzed the true meaning of evaluated data with almost no deeper examination of mathematical and physical background of this method under conditions of nonisothermal study.

The purpose of this paper is to examine the eqs. (2-4) in more details investigating mathematical circumstances that are purposeful and serviceable for realistic applications as well as analyzing the possible impact of the individual terms involved, namely the model of reaction mechanism, $f(\alpha)$ (with various meanings of the degree of conversion, α), the rate constant, $k(T)$ (and associated activation energy, E), heating rate, β, and its cooling "opponent" version (needing to include a thermodynamic driving force for the melt undercooling, ΔT, as a supplementary term) and, before all, the connotation of characteristic "maximum" temperature, T_m , in literature [6-19] habitually substituted by the temperature corresponding to the upper limit of an experimentally measured apex of a DTA peak, T_p.

2. Choice of reaction mechanism, $f(\alpha)$

It was shown that the Kissinger equation holds for any kinetic model based on equation (1), which can be mathematically derived [3] and generally symbolized by $f(\alpha)$ [11] . However, despite the apparent linearity of the dependences, we should be aware that the sensitivity of the required linear plot is damped by the logarithmic scale involved and thus, the data may not be representative for reaction profile fortitude. The original derivation [4,5] is based on a simplest model of reaction order, n, (i.e., $(1 - \alpha)^n$) later added by nucleation-growth JMAYK model, exponent p, (i.e., $(1 - \alpha)$ $(\log (1- \alpha))^p$) [3, 8, 13, 14, 18, 19] ending with a logistic SB model, with two parameters, n and m, (i.e., $(1 - \alpha)^n \alpha^m$) [3, 19, 22, 23]. The evaluation, however, cannot fully discriminate the category of a model in question whilst the model itself affects the values of activation energies insignificantly. Moreover the revaluation is strictly dependent on the progressive shifts of T_m along with the increasing heating rate, which, for example, is not the case of crystallization of finemet-kind of metallic glasses with a specific nanocrystalline structure [25, 26], that follows the Atkins NNG model [27] of normal crystal growth. This subject became a popular theme of the Kissinger equation modification) [6-19] so that we are not going to review and undertake deeper analysis within existing literature. Other problems of legitimacy of eq. (1) suspiciously consisting the assumption of

separability $\{r(T, \alpha) = k(T). f(\alpha)\}$ and the applicability of Arrhenius equation $\{k(T) = A.\exp(-E/RT)\}$ is dealt with elsewhere [3, 28-30].

3. Effect of temperature change focused on cooling applications

A number of recent applications of the Kissinger equation have been concerned with a nonisothermal crystallization of melts upon cooling, where temperature decreases with time giving rise to negative values of β which, factually, is not permitted within the validity of eq. (3). Mathematically, for the case of heating the left hand side in eq. (5) is positive (and a regular chemical process possess thus positive values of A and E) while on cooling it becomes negative. There is arising a equation whether the procedure of reversing the signal side would be legitimate. Regarding eq. (2) its sufficient condition is a positive value specifying the rate maximum in which, T_m, points upwards. On the other hand this equation can be modified even for a reversing signal on cooling

$$d(d\alpha/dt)/dt = d\alpha/dt \; [- B/T^2_m \; dT/dt \; - df(\alpha_m)/d\alpha \; A \; \exp (-B/T_m)] = 0. \tag{7}$$

The function in the square brackets is a mirror image of eq. (2) subsisting the role of minimum and thus yielding downward oriented peak. This requirement contradicts the fundamental meaning of the basic rate equation eq. (1) as well as the experimental observations of solidification kinetics. This case was thoroughly analyzed and modeled by Vyazovkin [31] showing that the simulated data provided mistaken and almost absurd results.

4. Revised equation when involving melt undercooling, ΔT

It follows that the rate constant written in the form standard exponential equation authorizes its application at the heating mode, only. For a more rigorous derivation we have to employ a modified rate equation where the simple form of eq.(1) is supplemented by additional term of a thermodynamic driving force mounting with the melt undercooling, ΔT [3, 32], as happen below equilibrium melting, T_o. In such a case we obtain

$$d\alpha/dt = K(T\Delta T) f(\alpha) \; = A \exp (-B/T\Delta T^2) f(\alpha) \; .\tag{8}$$

where $\Delta T = T_o − T$. Upon applying the same procedure as above we find analog of eq. (2) in the form

$$d(d\alpha/dt)/dt = d\alpha/dt \; (3\beta)/[T^2.(T_0-T)^2]. \; + \; + df(\alpha)/da \; A \exp \{-B/T(T_0-T)\} \;] = 0 \tag{9}$$

where β is now the rate of melt cooling. The

modified parallel of the Kissinger equation (5) than hold as

$$(3\beta)/[T^2_m (\Delta T)^2] = df(\alpha)/d\alpha \ (A/B) \exp \{-B/T_m (\Delta T)\} \ (10)$$

which enables to make a choice of the Kissinger-like plots (variants of eq (5) but involving a reciprocal combinations of T_m, T and ΔT). Its approval needs a range of experimental data, a preliminary test [33] shown, however, a limited range of linearity so that a more rooted mathematical and physical reasoning is necessary.

5. Degree of conversion and its meaning for homogeneous reactions and gradual transition processes

Degree of conversion, α, can be experimentally adjusted by various thermoanalytical measurements, an important point of which is the definition of the system under investigation. For example Svoboda et al [28] shown that the values of apparent activation energies, E, determined for glass transformation by the Kissinger method, were in a disagreement with the original values used for simulation, despite exhibiting apparent linear dependences. It was caused by the thermal history of the glassy samples and their evidently nonequilibrium (constrain [3,30,35]) states.

Another disturbing effect can be expected when studying variant processes of melting in multi-phase diagrams [35]. For example a *nonisothermal* degree of conversion, λ, can be introduced in the form [36]

$$\lambda = \alpha \ \lambda_{eq}(T), \tag{11}$$

where α represents the classical ´isothermal´ degree, and $\lambda_{eq}(T)$ represents the *equilibrium* degree of conversion for a given temperature T (so called equilibrium background), i.e. the degree thermodynamically pushed toward the end of the process. The nonisothermal rate equation, $d\lambda/dt$, is then given as a two-part sum

$$d\lambda/dt = \ \alpha \ (d\lambda_{eq}/dt) + \lambda_{eq} \ (d\alpha/dt), \tag{12}$$

which in the logarithmic form reads

$$d \ln \lambda/dt = \ (d \ln \lambda_{eq}/dt) + (d \ln \alpha/dt). \tag{13}$$

Upon the substituting (d ln λ_{eq}/dt = β. d ln λ_{eq}/dT) we obtain the expression for the maximum of nonisothermal rate (dλ/dt = max)

$$d^2\lambda/dt^2 = (d\lambda/dt). \ [\beta \ (d \ln \lambda_{eq}/dT) \ +$$
$$(d \ln \alpha/dt)] + \lambda.(d^2 \ln \alpha/dt^2) = 0. \tag{14}$$

The term λ_{eq} can be derived on the basis of an experimentally measured property Z (e.g. enthalpy) [36], the observation of which starts with the initial value, Z_o, attaining at the end of the process its maximum value, $Z_¥$, while for an isothermal course accomplishes its intermediate value $Z_{eq}(T)$

corresponding to the equilibrium at given operation temperature, T so that $\lambda_{eq}(T) = (Z_{eq}(T)-Z_o)/(Z_¥-Z_o)$. The further analysis towards the Kissinger-like plot is more complicated, the detailed solution of which falls beyond the concept of this contribution.

6. Characteristic temperature resolution of maximum rate from the apex of a DTA peak

Original 1957 Kissinger derivation starts from the temperature distribution in the differential thermal analysis specimen holders obeying the general heat flow equation (see eq.(1) in the original Kissinger´s paper [5])

$$\partial T/\partial t – (k/\rho c)\nabla^2 T = (1/\rho c)(dq/dt) \tag{15}$$

where (dq/dt) is the rate of heat generation due to a chemical reaction. Kissinger assumed conditions where the temperature of the outside of the holder rises at a linear rate, Φ (in our above symbolic, β), the solution of which is expressing the temperature at the center of the sample in the form (see eq.(3) in the original [5])

$$T_c = T_h + \Phi t \ – f(dq/dt) \tag{16}$$

where f (dq/dt) is a function of the reaction rate (including also any secondary effects of the reaction).

The differential temperature, θ, is the difference in temperature of the centers of the two samples. According to Kissinger [5] this difference, θ, is then given by

$$q = f(dq/dt)_{sample} – (\rho c/k)(\Phi a^2/4)_{reference} \tag{17}$$

and after the differentiation with respect to time (see his eq.(6) [5]) reads

$$dq/dt = f´(dq/dt)(d^2q/dt^2). \tag{18}$$

Eq. (18) (and eq. (6) in ref.[5]) states that the peak differential deflection occurs when the reaction rate is a maximum.

This approach, however, evidently ignored the effect of true heat transfer, which is responsible for the DTA peak mounting, and which apex, T_p, is affected by the sample heat inertia [31-33]. According to the equation originally derived by Vold almost ten years earlier (see her Eq. (5) in [40]) than that by Kissinger [5], we can ensue the Vold´s equation [40] as

$$-dq/dt = -(K/C_s)q + (1-C_r/C_s) \beta + (dq/dt)/C_s + \Delta K(T)/C_s \tag{19}$$

The symbol *K* is the instrumental constant, C's are heat capacities of the sample (s) and reference (r) and $\Delta K(T)$ reflects the difference between heat transfer conditions between the sample and the reference, so that

$$dq/dt – (Cs/K)d^2q/dt^2 = (d^2q/dt^2)/K, \tag{20}$$

which design is in contrary to the Kissinger´s final

eq.(6) in [5] (above eq.(18)).
    Substituting

$$(\mathrm{d}q/\mathrm{d}t) = H.(\mathrm{d}\alpha/\mathrm{d}t) \qquad (21)$$

where H is the reaction enthalpy change corresponding to the amount of sample we obtain the eq.19) but in the form

$$-\mathrm{d}q/\mathrm{d}t = -(K/C_s)q + (1-C_r/C_s)\beta + H(\mathrm{d}\alpha/\mathrm{d}t)/C_s + \Delta K(T)/C_s \quad (22)$$

so that after the differentiation we have

$$- \mathrm{d}^2q/\mathrm{d}t^2 = -(K/C_s)(\mathrm{d}q/\mathrm{d}t) + (H/C_s)(\mathrm{d}^2\alpha/\mathrm{d}t^2). \qquad (23)$$

For the extreme of a DTA peak, T_p, $(\mathrm{d}q/\mathrm{d}t = 0)$ we find

$$(C_s/K)(\mathrm{d}^2q/\mathrm{d}t^2) = -(H/K)(\mathrm{d}^2\alpha/\mathrm{d}t^2)$$
$$\text{Þ} \quad \mathrm{d}^2\alpha/\mathrm{d}t^2 = -(C_s/H)(\mathrm{d}^2q/\mathrm{d}t^2) \qquad (24)$$

and for the inflection points $(\mathrm{d}^2q/\mathrm{d}t^2 = 0)$ of a DTA peak we similarly determine from eq.(23) relation

$$\mathrm{d}^2\alpha/\mathrm{d}t^2 = (K/H)(\mathrm{d}q/\mathrm{d}t), \qquad (25)$$

explicitly showing the misfit between, T_m and broadly implemented value of the DTA apex, T_p [5-19].

The difference between temperature of extreme of a DTA peak and the temperature of a maximum reaction rate was already noted e.g. by Chen and Kirsh [41], Boerio-Goates and Callen [42], and exclusively shown in our recent paper [39]. A portrayal of such a DTA peak assessment is schematically exemplified in Fig 1.

Despite a long lasting history of kinetic evaluation it is clear that such an important part of DTA peak analysis has been overlooked at everyday applications. It is possibly caused by the obvious methods simplicity, which provides easy publishable values of activation energies. It is surprising that anybody who evolved various alternatives of the Kissinger method [6-19] did not find any reasons for its criticism.

7. Conclusion

The widespread application for an uncomplicated kinetic data resolution by the famous Kissinger method [4, 5], which received as many as 4461 responses [21], includes, however, a key error already rooted in the equation original derivation [5] omitting the factual effect of heat inertia [37-39]. This crucial mistake affecting the true temperature of maximum reaction rate has been lengthily put into everyday operation by various scientists who are not cognizant that such a widely used characteristic value for the maximum of reaction rate, T_m, is not identical with the maximum of DTA peak deviation, T_p. Associated application apparently results in changes of the numerical values of resulting activation energies, which misfit has no impact on the paper publication capability as the unchallenging value of activation energy has, in reality, no particular meaning [2, 28, 30]. Thus we are not convinced that our notification of this error will be accepted with a supporting applaud
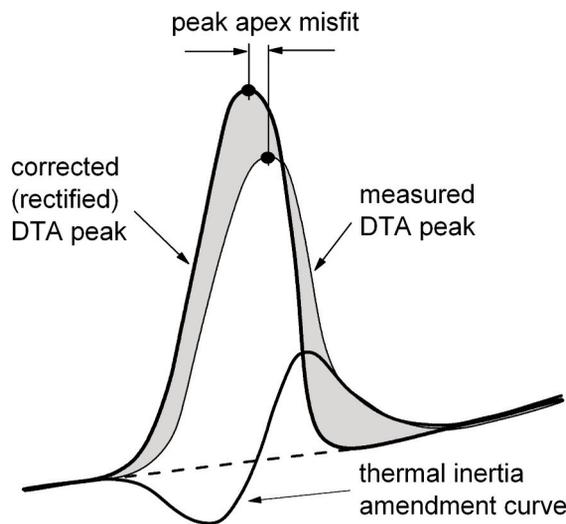

Figure 1. *Illustrative evaluation of advanced analysis of a DTA peak when incorporating the impact of thermal inertia of the sample showing the discrepancy between positions of the resulting peak maxima. A schematic portrayal of DTA peak (thin line) monitored by standard measurement obtained under heating for the separate cells is shown in contrast with its rectified form (thick line) obtained after the application of DTA correction (see text) for the sample thermal inertia, the effect of which is revealed at bottom as the s-shaped curve. Shaded sections display the difference on the gradual built up (left) and subsequent extinction (right) of the peak shape, the areas of which are identical in their final account (s-shape curve is symmetrical) thus affecting kinetics (gradual grows-reaction degree) but not calorimetry (total area-enthalpy).*

because it factually means that copious articles so far published cover incorrect data.

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