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Letter to the Editor

MYSTERY OF DERIVATIVES IN THE NON-ISOTHERMAL RATE EQUATION: NEED FOR A ROUND-TABLE DISCUSSION

Despite the fact that the degree of conversion, α, is not considered to be a state function independent of reaction pathway, Błażejowski stated in a recent article [1] that the application of mathematical rules concerning the existence of a total differential with regard to the function

$$\alpha = \hat{\alpha}(t, T) \tag{1}$$

confirms that the equation

$$d\alpha = (\partial\alpha/\partial t)_T dT + (\partial\alpha/\partial T)_t dt \tag{2}$$

is valid for expressing reaction kinetics under non-isothermal conditions. It seems rather an ultimative statement and the long-lasting discussion [2–23] initiated by MacCallum and Tanner [2] fifteen years ago is again in the state of an endless exchange of opinions. I have already reciprocated Letters to the Editor on this subject, accidently along with another Polish scientist, Norwitz [3] (however not cited in ref. 1); which, at least, makes me question editorial policy, sometimes requiring attention to be paid to a more careful reviewing of articles submitted, and also to a possible development of certain rules (standards) for repeatedly publishing general and often widely rediscussed problems [23]. This is not only the case for thermoanalytical journals, since a similar form of this equation (1) hit the pages of Journal of Non-Crystalline Solids [11,12] in the form of a modified kinetic equation introduced for crystallization kinetics [9–12,22].

In this context I remember the article "Study on non-isothermal transformation by DSC" [5] which I received to review in 1983. It was a well-written study having a high technical content and clearly developed mathematics. However, from my personal point of view, I considered the inherent eqn. (1) to be a particular solution of the general differential (rate) equation: $\dot{\alpha} = \hat{\alpha}(\alpha, T)$ (for given $T = \hat{T}(t)$). This equation (1) implies that the state of the system, α, is merely dependent on the reaction time, t (from $t = 0$ for $\alpha = 0$) and on the temperature T (for α), regardless of the system itself and is equally valid whether or not the sample is present, which is a logical nonsense. Although impressed by the experimental evidence in ref. 5, supporting the apparent validity of partial derivatives in eqn. (2), I recommended its publication after certain reconsiderations with respect to the past literature [2–23] which was accepted but, unfortunately, has not been accomplished yet. Articles made in such a discussive way [1,12,21,23–26] are appreciable, since they stress the existing discrepancies inherent in non-isothermal kinetics, but should not be made for the purpose of extending the volumes of scientific journals.

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Very recently, Romero Salvador et al. [27] assumed that the α–t relation can be obtained through the integration of an otherwise basic form of the rate equation arriving at a modified form of eqn. (2) which can be accomplished by the substitution for the reaction rate r ($= \mathrm{d}\alpha/\mathrm{d}t = k_{(T)}\mathrm{f}(\alpha)$), applying rules coherent from eqn. (1)

$$\mathrm{d}\alpha/\mathrm{d}t/\mathrm{f}(\alpha) = \mathrm{d}\left[\int k_{(T)}\mathrm{d}t\right]/\mathrm{d}t + \mathrm{d}\left[\int k_{(T)}\mathrm{d}t\right]/\mathrm{d}T\mathrm{d}T/\mathrm{d}t \tag{3}$$

This procedure, however, is similarly misleading for deriving a corrected form of non-isothermal rate equation, $r_{\text{non-iso}}$, to that already discussed in refs. 3 and 16, i.e.

$$r_{\text{non-iso}} = r_{\text{iso}}[1 + E/RT(T - T_0)] \tag{4}$$

Although the apparent validity of eqn. (4) for non-isothermal conditions [27] is supported by a good agreement of the theoretically calculated iso and non-iso rate data, its physical meaning again remains questionable. Misunderstanding may already originate from the incorrectly cited and inadequately searched literature given in ref. 27. This, however, is not unique since an unsatisfactory reference background is often met in many contemporary studies [23] resulting from the overwhelming number of (yet increasing) publications. One should, at least, take the trouble to look through the past issues of the journal in which the article is being considered for submission.

During my last meeting with Professor Jimm R. MacCallum in Prague, 1981, we came to a conclusion that regardless of our opposing opinions, we need to have a joint session together with some other interested scientists to finally clarify our standpoints. The grounds for the further planning of a round-table discussion as a major activity during a thermoanalytical conference was thus initiated [28]. In this sense I would like to invite all thermoanalysts engaged in the study of non-isothermal kinetics to take part in the 8th ICTA '85 workshop on *current problems of non-isothermal kinetics* and to submit a written question (of about 50 words maximum) which will be answered through a preselected board of distinguished scientists (and later, possibly, published as a separate issue of Thermochimica Acta). To guide interested kineticists in clarifying the above problem (which belongs to many noteworthy problems in non-isothermal kinetics [1,23]), I list below the pertinent literature either supporting [1–13,27] or rejecting [8,14–23] the validity of eqns. (1) and (2).

In a similar way the receipt of questions for the other thermoanalytical workshops on: energy conversion and non-stoichiometric oxides, computation and databanks, less-common techniques, and education and instrumentation are sincerely welcome to make a profitable discussion during the 8th ICTA '85 in Bratislava (August 19–23, 1985).

JAROSLAV ŠESTÁK
(*Bratislava, Czechoslovakia*)

LIST OF SYMBOLS

α	dimensionless extent of reaction
T	temperature
t	time
$k_{(T)}$	exponential (Arrhenius) rate constant
$f(\alpha)$	mathematical model of reaction mechanism
E	activation energy
d, ∂	derivatives
r	reaction rate

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