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Letters to the Editor

THE KINETIC EQUATION UNDER NON-ISOTHERMAL CONDITIONS

Dear Sir,

The article by MacCallum and Tanner[1] certainly belongs among the most cited and discussed subjects in the field of kinetics. This fact may indicate either its extraordinary nature or insufficiently reasoned reaction by its readers. Therefore, I would like to advocate the creation of a permanent column for the presentation of readers' opinions, questions and critical notes on controversial non-isothermal kinetics. This, in fact, was the reason for my writing a critical review "Philosophy of non-isothermal kinetics" in the form of a dozen questions and answers[2].

The purpose of my present communication is also to comment on the recent note by Norwisz[3]. In particular, even if the premises on which eqns. (1) and (2) of ref. 3 are based are not considered incorrect (see ref. 4, p. 448), the resulting eqn. (15) indicates that a given process would apparently proceed about an order of magnitude faster under non-isothermal than under isothermal conditions[5]. Such a great discrepancy, however, was not evidenced experimentally. Another unmentioned consequence[5] would be the effect of the equilibrium temperature, T_0. For the actual temperature, T, approaching the equilibrium temperature ($T \rightarrow T_0$), eqn. (15) becomes an ordinary kinetic equation. This is in contradiction of the known effect accounted for as the proximity to equilibrium (see ref. 4, p. 478). For more details, I would refer interested readers to our mathematical analysis published elsewhere[5]. However, I would draw attention to some other urgent points implicitly hidden in the abovementioned discussions.

In my opinion, we sometimes pay too much attention to detailed mathematical manipulation whereas too little is given to its logistic background. A good example of this is the habitual publication of numerical values of the so-called activation energies down to decimal places, or their mutual comparison in order to compare the accuracy of different methods of kinetic data evaluation. Sometimes, an acquaintance with some of the popular books on statistics[6] would be advisable.

Citation policy is also worth noting because the note by Norwisz[3] contains only two references, although additional ones could easily be found by searching earlier issues of *Thermochimica Acta* and *Nature*, the two journals cited in ref. 3. It clearly shows either that there is too little information given in the present overcrowded literature, or that not much time (or interest) is devoted by authors to a proper literature search. In this case, the articles on the calculation of the p(x) function, published in *Thermochimica Acta* and *Journal of Thermal Analysis*, may serve as an additional warning[2].

In this light, the article by MacCallum and Tanner[1] should not be condemned as completely erroneous because it demonstrates well the value of bringing some not yet clear topics of non-isothermal kinetics to our attention (see ref. 4, p. 448). A seriously guided discussion[7] would have been valuable for a widespread thermoanalytical society and could have avoided the eight years delay in replying, which is not the fault of Norwisz, but the result of our publishing policy. All this supports my initial proposal to start the discussions on a more controlled level[2].

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REFERENCES

1 J. P. MacCallum and J. Tanner, *Nature*, 225 (1970) 1127.
2 J. Šesták, *J. Therm. Anal.*, 16(2) 1979.
3 J. Norwisz, *Thermochim. Acta*, 25 (1978) 123.
4 J. Šesták, V. Šatava and W. W. Wendlandt, *Thermochim. Acta*, 7 (1973) 333.
5 P. Holba and J. Šesták, *Z. Phys. Chem. N.F.*, 80 (1972) 1.
6 H. Swoboda, *Knaurs Buch der Modern Statistik*, Droemer Knaur, München, Zürich, 1971.
7 J. P. MacCallum, private communication.

Dear Sir,

In reply to the letter from J. Šesták concerning the paper "The kinetic equation under non-isothermal conditions", I would like to make clear my attitude towards some of the remarks presented in it.

(1) Treating mathematics as an instrument for exposing the relations obviously not arising from the assumptions made, in the paper cited I attempted to verify the assumptions made for the reaction's kinetics by such a transformation of eqn. (3) from ref. 1 in order to achieve a form provable by experiment. However, the experimental proof of the equation obtained was not the subject of the paper. The minute amount of literature cited stems from the fact that its only purpose was to note the differences in opinion concerning the course of reaction under the linear temperature increase.

(2) The consistency obtained between eqn. (12) from ref. 1 and eqn. (A 19) from ref. 2 shows that the way of reasoning and the doubts concerning the course of reaction under the conditions of linear temperature increase were similar. I was unaware of the earlier paper[2], otherwise I would never have sent the paper in this form for publication. However, it should be noted that the method presented in ref. 2 is based on the particular form of the function $f(\alpha) = (1 - \alpha)$, the so-called reaction order equals one, whereas in ref. 1, this limitation is irrelevant.

(3) The reproach by Šesták, relating to the approximation of eqn. (15) from ref. 1 or eqn. (A22) from ref. 2 for $T \rightarrow T_0$ has also been somewhat difficult for me. This inconsistency is evident proof that the system of assumptions made is contradictory. I did not discuss this problem thoroughly since I expected that the assumption $(\alpha)_{T=T_0} = 0$ for $t \in (0, \infty)$ (where T = temperature, t = time and α = extent of reaction) is of no great practical importance. In the light of the present discussion, and chiefly of the information presented by Šesták and my own reply, it is suspected that the sphere $\alpha = \alpha(T, t)$ does not exist, i.e. that α is not a function of the state, as is, for example, enthalpy, but is more likely a function of the method, as is for example, heat.

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REFERENCES

1 J. Norwisz, *Thermochim. Acta*, 25 (1978) 123.
2 P. Holba and J. Šesták, *Z. Phys. Chem. N. F.*, 80 (1972) 1.