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NONISOTHERMAL KINETIC ANALYSIS-SOME CURRENT PROBLEMS

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ABSTRACT

The author presents a review article concerning some aspects of nonisothermal kinetics as they are reflected by the literature of the last three years.

This short review article aims to present some theoretical and methodological problems concerning nonisothermal kinetics of heterogeneous processes as they have been raised in the literature in the period 1985-1988 between the 8th and 9th ICTA Congresses in Bratislava and Jerusalem.

To begin with, one has to mention an attempt at a new classification of the methods used to evaluate the nonisothermal kinetic parameters [1] . The classification is based on the extent of the (α, t, T)interval and includes three classes of methods namely:

- methods which use the integration over all the values of (α, t, T); notation ——),
- methods which use integration over small intervals of (α, t, T); notation –(–)——,
- methods which use point values of the experimental data (α, t, T); notation –•– .

A succession of articles written by Vyazovkin and Lesnikovich, impressive by the trend to modern methods of data treatment, deals with the application of mathematical statistics to nonisothermal kinetics [2-6].

To increase the unambiguity of the solution of the inverse problem of nonisothermal kinetics[from the experimental data $\alpha(t)$, $\dot{\alpha}(t)$ and $T(t)$ to evaluate the nonisothermal kinetic parameters] the authors suggest, for instance in the case of the Coats-Redfern method, a variant of nonlinear regressional analysis to be used. Special emphasis is given to the fact that the improvement of the methods to evaluate the nonisothermal

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kinetic parameters requires careful consideration of the statistic aspects connected with their application[2].

Concerning the sensitivity of the method in evaluating the nonisothermal kinetic parameters to the form of the conversion function, the authors suggest the value of the curvature of the line (residual dispersion, reaction order) at the point of minimum as a numeric characteristic of it[3].

A unified approach of the conversion function analysis was equally considered by the authors[4]. They suggest the treatment of the whole set of conversion functions as a space. The analysis of such a space provides four classes of conversion functions, characterized by similar properties and close values of the nonisothermal kinetic parameters. The solution of the inverse problem of nonisothermal kinetics consists in the unambiguous finding of the class of conversion functions.

The adequate description of heterogeneous reactions using the methodology of formal nonisothermal kinetics was further considered by the same authors [5]. They emphasized the contradiction between the certitude of the reaction mechanism and the incertitude of its appropriate description a contradiction which cannot be solved in the framework of the conventional methodology of treating the inverse problem of nonisothermal kinetics. As an alternative to the conventional methodology based on the unambiguous description principle, a methodology based on the complementarity of the conversion functions principle is suggested. The last one is advantageous in obtaining information concerning the investigated process from the set of ambiguous solutions.

Concerning the complementarity of the conversion functions, the authors show that due to the incomplete descriptive character of a unique conversion function for a given process one can always find a set of conversion functions which allow its complete description. Thus the individual conversion functions contain only partial information concerning the investigated process.

According to the complementarity principle the conversion functions which formally describe a given process should be complementary rather than competitive. Thus, to solve the above mentioned contradiction, as an alternative to the conventional methodology one has to synthesize a formal picture of the investigate process from the information on its particular aspects as given by the competitive conversion functions.

Based on a comparison between the conventional and non-conventional methodologies, the authors conclude that the latter provides greater amounts of information[6].

By applying a methodology based on the principle of complementarity to solve the inverse problem of solid-phase reaction kinetics, one must mention an interpretation of the applicability of the KEKAM (Kolmogoron-Erofeev-Kazeev-Avrami-Mampel)equation to describe complex processes[7] and a generalized kinetic description using a spectrum of conversion functions[8].

In the author's opinion, a concept similar to the concept of complementarity was formulated earlier in 1985, by Tanaka, at the workshop dedicated to current problems of kinetic data reliability evaluated by thermal analysis at the 8th ICTA in Bratislava[9]

Concerning the statistical treatment of data in nonisothermal kinetics one must mention the paper of Neag and coworkers[10] devoted to statistical evaluation of non-isothermal decomposition kinetics who showed that the values of the nonisothermal kinetic parameters for the decomposition of AIBN(2,2'-azobis-izobutyronitrile) are insensitive to the differential or integral character of the method used to obtain them.

An analysis of the dependencies between nonisothermal kinetic parameters and conversion functions allowed Vyazovkin and Lesnikovich to develop a mathematical procedure based on Jacobi's matrix for evaluating the numbers of independent kinetic parameters and conversion functions[11]. It has been found for instance that in the Šesták-Berggren equation it is not possible to evaluate more than five kinetic parameters. As far as the conversion functions are concerned, the real dimension of their space is twice as small as their total number. Thus some of the conversion functions could be represented as linear combinations of independent functions. Obviously, only the linearly independent functions contain valuable information concerning the investigated process, as they characterize some of its particularities. The authors state that this in an argument for the non-conventional methodology to solve the inverse problem of nonisothermal kinetics.

As far as the compensation effect is concerned, we may mention an article by Agrawal [12] . According to this author, the criterion for the existence of a true kinetic compensation effect consists in the existence of an isokinetic temperature i.e. at an intersection point on the Arrhenius straight lines. In the cases where the compensation effect is an apparent one such an intersection point cannot be put in evidence. Such a standpoint seems to be similar to that expressed by Flynn who suggested that instead of plotting the activation energy E against ln A(A is the preexponential factor) plots of ln k against 1/T should be checked for intersection at a single isokinetic temperature[9]. Agrawal's criterion was discussed by Šesták[13] and criticized by Zsako and Somasekharan[14] who expressed doubts on its correctitude.

Although an old problem the approximate calculations of the temperature integral still concerns research workers interested in nonisothermal kinetics. Agrawal suggests the following approximation of the temperature integral[15].

$$\int e^{-\frac{E}{RT}} dT = \frac{RT^2}{E} \left[\frac{1-2\,\frac{RT}{E}}{1-5\,(\frac{RT}{E})^2} \right] e^{-\frac{E}{RT}} \qquad (1)$$

Another four approximations of the temperature integral have been proposed by Urbanovici and Segal[16]. Popescu and coworkers presented an analysis of some possibilities to solve the temperature integral[17] as well as a comparison of the temperature integrals corresponding to linear and nonlinear heating programs[18].

The possibilities of evaluating the nonisothermal kinetic parameters using the fundamental equation of nonisothermal kinetics have been analysed by Urbanovici and Segal[19]. Some critical considerations concerning the use of the conversion degree in the rate equations in comparison with the extensive variables weight and radius of the contracting sphere are given by Fătu and Segal [20].

As far as special heating programms are concerned, a program which ensures a linear dependence between the conversion degree and the temperature should be mentioned [21].

Considering the heating rate as a variable in nonisothermal kinetics, using integration over small temperature intervals and several heating rates Urbanovici and Segal developed some methods to evaluate the nonisothermal kinetic parameters [22-24]. The same authors worked out a new iterative "classical" (with constant kinetic parameters and invariable conversion function) method to evaluate the nonisothermal kinetic parameters [25] and a simple method to evaluate the "reaction order" of heterogeneous decompositions under nonisothermal conditions [26] .

Based on some experimental data concerning the dependence of the nonisothermal kinetic parameters on the conversion degree, new equations explicitly showing this dependence have been worked out [27-29]. The last work concerning this topic was presented at the 9th ICTA in Jerusalem [30]. The author cannot consider this paragraph as complete without mentioning a critical analysis concerning the methodology of studying reaction kinetics by thermal analysis by Křiž and Šesták [31] as well as a work dedicated to some pitfalls connected with nonisothermal kinetics and some rules to overcome them [32].

At the above mentioned workshop devoted to nonisothermal kinetics it was commented that a task for the ICTA kinetics committee is to determine which equations are correct under which conditions [9] . The final part of this short article is devoted to some partial answers to this fundamental problem of nonisothermal kinetics [33-36] namely the derivation of correct kinetic equations capable of describing the evolution of the investigated physical or chemical system. Taking into account the lack of an advanced theory, such a derivation has to be performed using as starting point isothermal kinetic equations. Using such conditions one has to assume the equality between the values of the nonisothermal kinetic parameters and the corresponding values of isothermal kinetic parameters. In order to derive nonisothermal kinetic equations a classical nonisothermal change (CNC) has to be operated in the corresponding isothermal kinetic equation. This consists in the substitution of T=const in the isothermal kinetic equation with $T=\theta(t)$. The CNC cannot be performed in any isothermal kinetic equation.

The isothermal kinetic equations which admit a CNC have been called primary. Thus we have:

- primary isothermal differential kinetic equation (PIDKE)
- primary isothermal integral kinetic equation (PIIKE)

As in the case of a complex system it is not possible to decide whether an isothermal kinetic equation is primary or not, one has to postulate the primary character i.e. we can distinguish between

POSTULATED - PIDKE (P-PIDKE)

and

POSTULATED - PIIKE (P-PIIKE)

As shown by us[36] it is recommended to consider as primary, a kinetic equation in which a minimal number of mathematical operations in isothermal conditions have been performed.
This requirement is fulfilled for instance by the equation:

$$\frac{d\alpha}{dt} = A\, f(\alpha)\, e^{-\frac{E}{RT}} \qquad T = \mathrm{const} \qquad (2)$$

but it is not fulfilled by the equation:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = A\, e^{-\frac{E}{RT}}\, t \qquad T = \mathrm{const} \qquad (3)$$

due to the fact that the integration under isothermal conditions is incompatible with the nonisothermal character of the system.
Thus, it seems that isothermal differential kinetic equations should be preferred for postulation as primary. This conclusion, in agreement with an earlier suggestion by Flynn [9], is supported by applying a model which divides the (α,t) curve into infinitesimal isothermal portions (MIIP).

The authors emphasize that in order to derive correct kinetic equations one has to take into account the fact that under isothermal conditions t and T are independent variables while in nonisothermal kinetics they are dependent ones. In such conditions the discussion concerning the existence of the total differential:

$$d\alpha = \left(\frac{\partial\alpha}{\partial t}\right)_T dt + \left(\frac{\partial\alpha}{\partial T}\right)_t dT \qquad (4)$$

initiated by MacCallum and Tanner[37] is in our opinion meaningless. The error of the above mentioned authors consists in the assumption that in nonisothermal conditions a relationship of the form:

$$\alpha = U_N(T,t) \tag{5}$$

with T and t as independent variables is valid(N-nonisothermal). By differentiating, from (5) we obtain:

$$d\alpha = \left(\frac{\partial U_N}{\partial t}\right)_T dt + \left(\frac{\partial U_N}{\partial T}\right)_t dT \tag{6}$$

a relationship which contains the partial derivative at t=const $\left(\frac{\partial U_N}{\partial T}\right)_t$ which is meaningless. A correct solution of the problem consists in introducing into (5), $\theta(t)$ instead of T, thus

$$\alpha = U_N(\theta(t),t) \tag{7}$$

The differential of (7)

$$d\alpha = \frac{\partial U_N}{\partial t} dt + \frac{\partial U_N}{\partial \theta} \frac{d\theta(t)}{dt} dt \tag{8}$$

does not contain any term at t=const.

To complete this paragraph one must mention the papers of Šesták and Kemeny in which they analysed some problems concerning the kinetics of crystalization described mainly by the JMAYK equation[38] as well as the conditions for a generalization of the laws describing nucleation and growth controlled transformations[39]. One must similarly mention analyses of the applicability of the Avrami-Erofeev equation in nonisothermal kinetics[40] and of the complex reactions which occur in nonisothermal conditions, followed by TG and DSC instruments[41].

At the workshop devoted to nonisothermal kinetics held during the 9th ICTA in Jerusalem, the author of this article expressed the opinion that the field is passing through a crisis. This standpoint was not shared by other scientists such as J.Šesták. No matter if the crisis is a true or apparent one the author express his hope that the work developed in the field, partially mentioned in this article as well as further work will contribute essentially to emerge from it and to transform the nonisothermal kinetics into a valuable instrument for the investigation of chemical reactivity tightly anchored in general chemical kinetics principles.

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