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Note

40 YEARS OF THE VAN KREVELEN, VAN HEERDEN AND HUTJENS NON-ISOTHERMAL KINETIC EVALUATION METHOD

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ABSTRACT

Forty years of development of non-isothermal kinetics are critically reviewed. Some proposals concerning the correct evaluation of kinetic data are presented.

We consider it worth noting that it is the fortieth anniversary of the first attempt to evaluate collectively the kinetic data from a single non-isothermal run which was published by Van Krevelen, Van Heerden and Hutjens in 1951 [1]. This evaluation procedure formed the basis of the so-called integral methods [2] commonly used in thermal analysis (TA), in which the Arrhenius rate constant, $K(T) = A\mathrm{e}^{-x}$ $(x = E/RT)$, must be integrated under conditions of linear temperature increase, $\beta = \mathrm{d}T/\mathrm{d}t$. Because the integral $\int K(T)\mathrm{d}T$ cannot be expressed explicitly, the authors approximated it [1] obtaining a plot of ln $g(\alpha)$ against ln T. The function $g(\alpha) = \int \mathrm{d}\alpha/f(\alpha)$ is the so-called integral form of the kinetic model, $f(\alpha)$, assuming the validity of the basic kinetic equation, i.e. $\mathrm{d}\alpha/\mathrm{d}t = K(T)\ f(\alpha)$.

In the mid nineteen fifties, the two most cited methods of non-isothermal kinetics were introduced: the multi-run method of Kissinger [3] and the difference-differential method of Freeman and Carroll [4]. Since then, numerous evaluation methods have been published [2], the integral ones being the most convenient for simplified TA practice, as based on the early sixties work of Doyle [5]. The sensitivities of these methods were often compared [6] and the mathematical treatment was remanipulated producing the greatly simplified kinetic evaluation developed by Szako [7], MacCallum and Tanner [8] and Šatava [9]. This evaluated the straight line by plotting ln $g(\alpha)$ against $1/T$. This approach, however, approximated the function

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$\pi(x)$ in the integral kinetic equation $g(\alpha) = (AE/\beta R)\, e^{-x}[\pi(x)/x]$ to just $1/x$. Applying even higher mathematics, this most popular plot of $g(\alpha)$ against $1/T$ became equivalent to the abandoned treatment of Reich and Levi [10] published in the early sixties, in which it was assumed that $K(T)$ was constant and thus the term was put in front of the temperature integral. Such simplifications were, in fact, a return to the method of Coats and Redfern [11] who had approximated $\pi(x)$ more accurately by $(x-2)/x^2$. This more complicated formula was later improved by Gorbachev [12] who suggested a more convenient and sufficiently accurate approximation in the simple form of $1/(x+2)$.

Since then, considerable effort has been directed to the proper approximation of the $\pi(x)$ function to obtain as accurate a function as possible [2]. The exactness of this approximation was found to have an important influence on the shape of the calculated curve. Nevertheless, the impact of different statistical methods and, in particular, the use of computers to perform iterative procedures made further simplification of the $\pi(x)$ function unnecessary. Nevertheless, a major distorting effect remained resulting from an inappropriate application of the various kinds of regression analysis in the logarithmic scale [13]. In addition, the advent of computerized evaluation did not stop the search for further new evaluation methods, merely algebraic manipulations of the different forms of the kinetic equation.

Besides the already solved question of how to deal with the integrated form of the rate constant, we have to admit that there are other, not fully understood, problems in non-isothermal kinetics which can be ranked in two groups. First, there are the more general questions associated with either the differentiation of isothermal and non-isothermal reaction rates, as noted by MacCallum and Tanner in 1970 [14], or the mutual interdependence of kinetic parameters (pre-exponential factor, A, and activation energy, E) [6], sometimes called the kinetic compensation effect, as reintroduced by Garn in 1976 [15,16]. Although their solution seems clear to us when assuming all mathematical consequences [2], it remains a puzzle for the many scientists attempting to repeat it. We, however, wish to concentrate on the second group of problems connected directly with the kinetic data evaluation as discussed above, i.e.:

(i) how to properly distinguish between the kinetic models represented by the $f(\alpha)$ [17] and $g(\alpha)$ [9] functions;

(ii) how to determine the diagnostic limits of a formal multiexponent equation for the $f(\alpha)$ function of the form $\alpha^m(1-\alpha)^n$ or $(1-\alpha)^n \ln(1-\alpha)^p$ [18];

(iii) how to use the master plots for the determination of kinetic models [19,20]; and

(iv) how to refine the problem of simultaneous determination of the kinetic model and kinetic parameters from a single non-isothermal run [21].

It is known that integral methods are generally less sensitive in the determination of the kinetic model because of overlapping $g(\alpha)$ functions. On the other hand, differential methods seem to be more useful in distinguishing between individual kinetic models, $f(\alpha)$, but the sensitivity of these methods depends strongly on the noise content of the original data. Moreover, it is well known that numerical smoothing may lead to a certain distortion of the original curve and to a subsequent quality decrease in the kinetic information [22].

The kinetic model functions derived on the basis of physical-geometrical assumptions of regularly shaped bodies evidently cannot describe real heterogeneous systems. Therefore, it is possible to use any function satisfying the need of a simple mathematical description without demanding correlation to a real reaction mechanism. It can even be based on a modified concept of reaction order [23].

The main problem arises, however, from the mutual correlation of kinetic parameters defined by the exponential form of the rate constant. As with the evaluation procedure for isothermal kinetics, we are almost sure that kinetic parameters can hardly be ascertained from a single non-isothermal run. The value of the activation energy (independent of kinetic model [24]) should preferably be determined from a set of non-isothermal measurements taken at different heating rates. Such a value then enables us to estimate the kinetic model by simply plotting the term $(\mathrm{d}\alpha/\mathrm{d}t)\mathrm{e}^{x}$ against α, which gives the characteristic profile of the $f(\alpha)$ function [21]. Except for special diffusion-controlled processes, most reactions can be described in terms of three formulae of gradually increasing complexity [21,23] i.e. the so-called reaction order model, $(1-\alpha)^{n}$, the Johnson–Mehl–Avrami model, $n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}$, and the Šesták–Berggren model, $\alpha^{m}(1-\alpha)^{n}$, the characteristic profiles of which correspond to the above-mentioned plot.

An alternative method for the determination of a plausible kinetic model can be based on a modified *master plot* comparing the theoretical curves, $f(\alpha)g(\alpha)$, with the experimental ones obtained by plotting the term $(\mathrm{d}\alpha/\mathrm{d}t)\pi(x)T/\beta$ against α [25]. All the types of kinetic model are well separated (including diffusion ones) attaining the maxima when α reaches its characteristic value, for which a general condition can be described [25]: $-[\mathrm{d}f(\alpha)/\mathrm{d}\alpha]g(\alpha)=1$.

Since the first survey on non-isothermal kinetics published by Garn [15] and Flynn and Wall [26], publications dealing with non-isothermal kinetics [2,16,27–33] have laid more emphasis on phenomenological aspects. Therefore, it became necessary to resolve the existing discrepancy either by philosophically oriented reviews [34–36] or by the formation of the ICTA kinetic subcommittee and the kinetic workshops regularly held during the ICTA conferences [37,38]. In order to understand the inherent problems, we also must realize that there are neither isothermal nor non-isothermal kinetics: both are certain approximations of experimental conditions in which the real course of the sample temperature is represented by that of its surroundings. In this respect we have to look for an alternative experimental solution to match better the actual and programmed experimental conditions. Constant rate thermal analysis (CRTA) [39] seems to be one of the possible solutions, at least in providing information complementary [40] to traditional TA kinetic data. CRTA is also suitable for more sensitively distinguishing nucleation-growth processes [41,42].

In addition we have to realize that on the basis of simple TA experiment alone, it is not possible to construct a mathematical theory applicable to more sophisticated measurements. Therefore, formal kinetic theory [2,18,23] using approximate functions of $f(\alpha)$ and $g(\alpha)$ must be carefully correlated with the assumed reaction mechanism [43]. This problem is associated with the development of certain rules concerning the investigation and analysis of the course of the reaction so as to eliminate the effect of experimental conditions and thus to provide invariant values of the kinetic parameters. It is clear that the habitual repetition of the basic mathematical formulae, as well as the listing of well known tables of model $f(\alpha)$ and $g(\alpha)$ functions, is a waste of printed space. It is important to publish raw kinetic data in order to be able to validate the procedure used for the evaluation of the kinetic parameters.

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