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Note

KINETIC FUNCTIONS CANNOT BE DETERMINED FROM ANALYSIS OF DYNAMIC DATA

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Thanks to the introduction of modern thermoanalytical techniques, collecting kinetic data on solid-state reactions has become a major effort in chemistry, as reflected by the rapid growth of the specialised journal *Thermochimica Acta* [1]. It is increasingly popular to collect dynamic data, which are obtained under the condition of a fixed rate of temperature change—a condition which may be closely realised in modern scanning instruments. However, the debate is surfacing in regard to whether such data can be analysed to identify unambiguously the explicit form of the kinetic function, namely $\mathrm{f}(1-\alpha)$ appearing in

$$\mathrm{d}\alpha/\mathrm{d}t = \mathrm{f}(1-\alpha)\, Z \exp(-E/kT) \qquad (1)$$

where α is the fraction of the solid reactant which has been converted by time t, k is the Boltzmann constant, T is the temperature, and Z and E are Arrhenius parameters. Many ingenious methods have been proposed by which $\mathrm{f}(1-\alpha)$ as well as Z and E may be derived. These methods are based on either the differential eqn. (1) or its integral form. In this note I wish to reiterate the alternative view that the kinetic function usually should only be determined from isothermal data.

It has been suggested, based on actual experience of data analysis (e.g., refs. 2–6) and on an illustration by computer simulation, that the effect of $\mathrm{f}(1-\alpha)$ on the dynamic curve is inherently masked by that of T being a linear function of t [7]. Previously the ambiguity in $\mathrm{f}(1-\alpha)$ derived by applying in particular the integral method of Coats and Redfern [8] has been pointed out. Criado and Morales [9] deduced that the use of this treatment could lead to Avrami–Erofeev types of kinetic function being erroneously taken as $\mathrm{f}(1-\alpha) = 1-\alpha$. Their mathematical deduction was experimentally borne out by Dharwadkar et al. [10] who, moreover, found that the apparent value of E varied with the type of $\mathrm{f}(1-\alpha)$ chosen. This variation was subsequently explained theoretically by De Bruijn et al. [11].

Incidentally, we should note that Criado and Morales [9], among others, have conceived the integral form of eqn. (1) in the case of $\mathrm{f}(1-\alpha)$ being an

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Avrami–Erofeev type, as

$$\left[\ln \frac{1}{1-\alpha}\right]^{1/m} = \int_0^t Z^{1/m} \exp(-E/mkT)\,\mathrm{d}t \tag{2}$$

where $m = 2, 3$, or ... The integrand on the right-hand side looks doubtful, because Z must have the dimension of $[\text{time}]^{-1}$ if it is to be physically admissible. A similar mistake was made over 40 years ago by Wischin [12] in her classic study on nucleation during the thermal decomposition of $Ba(N_3)_2$ crystals. Equation (2) should read

$$\left[\ln \frac{1}{1-\alpha}\right]^{1/m} = \int_0^t Z \exp(-E/kT)\,\mathrm{d}t \tag{3}$$

Back to the methods of analysing dynamic data, let us now look at integral treatments other than that of Coats and Redfern. They seem to be [7] less accurate than the Coats and Redfern method, with the exception of the treatment due to Ozawa [13] in which, however, the kinetic function remains indeterminate.

Only derivative methods of analysis need now to be discussed. Among those which give $f(1-\alpha)$, the most accurate procedure is that proposed by Sharp and Wentworth [14], who rewrote eqn. (1) into the form

$$\ln \frac{\mathrm{d}\alpha/\mathrm{d}t}{f(1-\alpha)} = \ln Z - E/kT \tag{4}$$

By plotting the left-hand side against $1/T$ for different types of $f(1-\alpha)$, they identified $f(1-\alpha)$ as the type associated with the most linear graph. It is argued below that this procedure may not lead to the true kinetic function, for some functional types at least.

The types to be examined are again those of Avrami–Erofeev, namely

$$f(1-\alpha) = \left[\ln \frac{1}{1-\alpha}\right]^{1-1/m} (1-\alpha) \tag{5}$$

The argument is that the factor $[\ln 1/(1-\alpha)]^{1-1/m}$ in the above may become 'hidden'. Consider the integral form of the Avrami–Erofeev equation given previously in (3), in which the temperature integral can be approximated as [8]

$$\int_0^t \exp(-E/kT)\,\mathrm{d}t \approx \frac{kT^2}{\beta E}\left(1 - \frac{2kT}{E}\right) \exp(-E/kT) \tag{6}$$

where $\beta \equiv \mathrm{d}T/\mathrm{d}t$. Equations (3) and (6) show that

$$\left[\ln \frac{1}{1-\alpha}\right]^{1-1/m} \approx \left\{Z \frac{k}{\beta E} T^2 \left(1 - \frac{2kT}{E}\right) \exp(-E/kT)\right\}^{m-1} \tag{7}$$

Combining eqns. (5), (7) and (4), we get

$$\ln \frac{\mathrm{d}\alpha/\mathrm{d}t}{1-\alpha} \approx \left\{\ln Z + (m-1) \ln \frac{k}{\beta E}\right\} + (m-1)\left[2 \ln T + \ln\left(1 - \frac{2kT}{E}\right)\right] - m\left(\frac{E}{kT}\right) \tag{8}$$

Since both $\Delta \ln T$ and $\Delta \ln(1-2kT/E) \ll \Delta(1/T)$ for the same ΔT, in the usual case of $kT/E \ll 1/2$, and statistical scatter inevitably exists in experimental data, the linearity of the plot of the left-hand side against $1/T$ is insensitive to the magnitude of m, including in particular $m = 1$. It may thus be asserted that derivative methods of dynamic data analysis cannot distinguish among kinetic functions of different Avrami–Erofeev types ($m = 2$, 3, or ...) as well as that of first 'order' ($m = 1$). Furthermore, as is obvious from eqn. (8), E and to some extent Z so calculated will change with the m chosen.

The last aspect may, nevertheless, be exploited to advantage; a bad thing can sometimes be turned to a good thing. Let E_0 denote the value of E extracted from several isothermal curves, and E_{m} that from a dynamic curve using the 'm' suggested by isothermal analysis. The comparison of E_m with E_0 serves as a check on the chosen m. If the two values do differ significantly it is probably correct to re-analyse the isothermal curves with $m' \approx mE_m/E_0$. This way of estimating m' is valid because, as has often been found empirically (e.g. refs. 15 and 16), E_0 itself depends little on the selection of kinetic function.

To give kinetic function types with physical meanings m or m' can only be integers. Also 'there is theoretical justification for orders of reaction of 0, 1/2, 2/3 and 1 in solid-state kinetics' [8], but not for the 'order' n to take intermediate values. The procedure of fitting kinetic functions to isothermal or dynamic data by allowing continuous variations in m and n (e.g., ref. 15) is therefore likely to be dubious. When it is done and a strange value of m or n produced, we should instead analyse the reaction as multi-stage (after re-checking that the sample, if a powder, did consist of particles having fairly uniform shape). The practice of analysing data with the a priori assumption that a reaction 'order' exists seems to be even more unjustifiable. A recent example is met in ref. 16, where experimental dynamic data from the pyrolysis of anhydrous lead chalate were so analysed, giving $n = 0.4$ (and $E = 4.2900$ kcal mole^{-1}, implying a precision of 1 part in 10^5!). The result is significant only had the substance been known to melt before decomposing, as some secondary explosives do, so that the reaction has a homogeneous rather than a solid-state mechanism.

The opportunity may also be taken to reiterate the fact that the so-called "compensation effect" is a fiction resulting from the ignorance of additional factors affecting reaction speed or from the invalidity of the Arrhenius form on eqn. (1) [7].

The last point again concerns the validity of eqn. (1). Since 1970 several authors have contended that extra terms are needed on the right-hand side to account for the fact that not only t but also T are variables. Most recently, Błażejowski [17] provided a mathematically rigorous proof for the following replacement of eqn. (1)

$$\mathrm{d}\alpha/\mathrm{d}t = \mathrm{f}(1-\alpha)Z(1+E/kT)\exp(-E/kT) \tag{9}$$

starting, however, from the premise that

$$d\alpha = \left[\frac{\partial \alpha}{\partial t}\right]_T dt + \left[\frac{\partial \alpha}{\partial T}\right]_t dT \qquad (10)$$

whose soundness, he emphasised, was an assumption. The assumption is false because α is not a state function with t and T as independent state variables [7]. In general, fallacies or confusions will result if T is considered as a state variable in calculations or graph plottings in reaction kinetics, which is a study of time-dependent processes under far from equilibrium conditions. MacCallum in his latest paper [18] indicated that

$$-\frac{d[A]}{dt} = \text{isothermal rate} + \frac{E\beta}{2kT^2}[A] \qquad (11)$$

where [A] represents reactant concentration. His derivation involved the convenient condition that pressure as well as volume remain constant. More importantly, the concentration of a chemical species has meaning only in homogeneous reaction kinetics; for solid-state reactions $1-\alpha \neq [A]_t/[A]_0$. In either case, eqn. (11) is questionable as it predicts an increase of [A] for a sufficiently large rate of temperature drop ($\beta \ll 0$).

In conclusion, several of the current controversies pertaining to dynamic kinetic analysis have been touched upon in this note, but my central claim is that in general we cannot reliably determine $f(1-\alpha)$ from even low-scatter dynamic data. This claim was made based on empirical and synthetic-data evidence and has been substantiated here by analytical arguments. Isothermal data are indispensible despite their problem of zero-time inaccuracy. A minimum of two experiments is required in studying the kinetics of a (single) reaction: an isothermal one to identify the kinetic function, and a dynamic one to provide Z and E. Further, if a series of isothermal runs at different T is carried out, the results can be used to ascertain the invariance of $f(1-\alpha)$ over the temperature range and to give an E which may be compared with the dynamic value. The most complete investigation will require, in addition to these isothermal curves corresponding to $\beta = 0$, a number of dynamic traces at various heating rates. The effects of sample conditions and ambient atmosphere will also have to be looked into.

NOTE ADDED IN PROOF

In a recent paper [19], a theoretical justification was presented for the practice of determining the Avrami–Erofeev index, m, as the slope of $\ln(d\alpha/dT)$ vs. $1/T$ plot for $0 \leqslant \alpha \lesssim 0.2$ divided by the activation energy. The derivation of eqn. (8) and the discussions that follow in the present work in effect corroborate this justification since for small values of α, $\Delta \ln(1-\alpha)$ is not large and thus $\Delta[\ln(d\alpha/dT) - \ln(1-\alpha)] \approx \Delta \ln(d\alpha/dT)$ usually. It may be argued, however, that this method of determining the kinetic function seems to be superfluous and incomplete. The criticisms are (a) $f(1-\alpha)$ has to be known beforehand to be of the Avrami–Erofeev type, (b) E_0 also needs to be already found, and (c) later stages of the reaction kinetics are not analysed when m can change; in fact, often, m decreases as nucleation stops and only the growth of nuclei continues.

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