Thermochimica Acta, 110 (1987) 131–134
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE EVALUATION OF KINETIC PARAMETERS FROM NON-ISOTHERMAL EXPERIMENTS

TAMÁS KEMÉNY

Central Research Institute for Physics, P.O.B. 49, Budapest (Hungary)

ABSTRACT

The alternative evaluation of non-isothermal kinetics based on the modified form of the rate equation is discussed. It is shown to be equivalent to the assumption that the same equation for the transformed fraction holds under isothermal and non-isothermal conditions. It is definitely inapplicable to any problem where the transformed fraction is also dependent on the T(t) path.

INTRODUCTION

The general problem of non-isothermal kinetics has been extensively discussed in recent years (for references see ref. 1). Despite the fact that the correct procedure for evaluating non-isothermal experiments had been reviewed almost two decades previously [2], many publications taken the view of MacCallum and Tanner [3] and question the very foundation of this evaluation. Since it is felt that the radical consequences of the alternative formulation are not fully understood, they are briefly outlined in the present note. It is intended to show that this new formalism has an inevitable consequence: the transformed fraction should be independent of its thermal history; a claim which is hardly fulfilled by any problem usually investigated in thermal analysis.

ISOTHERMAL AND NON-ISOTHERMAL EVALUATION OF KINETIC PARAMETERS

The rate equation usually taken is

$$\frac{d\alpha}{dt} = f(\alpha)k(T) \tag{1}$$

where α is the transformed fraction, $f(\alpha)$ is a function characteristic of the

---

Thermal Analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.

0040-6031/87/$03.50

transformation mechanism and $k(T)$ is the temperature dependence which is usually believed to be of the form:

$$k(T) = Z\mathrm{e}^{-E/RT} \tag{2}$$

This equation is easily integrated when $T =$ constant to yield:

$$\mathrm{g}(\alpha) = k(T)t \tag{3}$$

The functions $\mathrm{f}(\alpha)$ and $\mathrm{g}(\alpha)$ are interrelated:

$$\mathrm{g}(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha'}{\mathrm{f}(\alpha')} \qquad \mathrm{f}(\alpha) = \left| \frac{\mathrm{dg}}{\mathrm{d}\alpha} \right|^{-1} \tag{4a, b}$$

While eqns. (1) and (3) are fully equivalent when $T =$ constant, it is quite clear that *both might not be simultaneously valid under non-isothermal conditions.*

The starting point of the usual formalism is the isokinetic hypothesis, i.e., the transformation *rate* is independent of its thermal history and is given by eqn. (1) under any circumstances. The transformed fraction, α, is calculated by the integration of eqn. (1)

$$\mathrm{g}(\alpha) = \int_0^t k[T(t')] \,\mathrm{d}t' \tag{5}$$

where α is clearly dependent on the whole $T(t)$ path. This means that the assumption of the existence of an $\alpha(t, T)$ function, i.e., a function which is supposed to predict the transformed fraction, if only the actual time, t, and temperature, T, are specified is fully incompatible with this formulation. It is also evident in eqn. (5) that the transformed fraction, α, depends on the time, t, exclusively through the upper limit of the integral. In this way the time derivative of the transformed fraction cannot yield anything else but eqn. (1); no doubts can be raised concerning the mathematical rule for the differentiation of implicit functions.

The alternative formalism suggested by MacCallum and Tanner on the other hand rejects the use of eqn. (1) under non-isothermal conditions. It is claimed that only the partial derivative, $\left.\frac{\partial \alpha}{\partial t}\right|_T$, is measured under isothermal conditions, therefore the actual rate in non-isothermal measurements is:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left.\frac{\partial \alpha}{\partial t}\right|_T + \left.\frac{\partial \alpha}{\partial T}\right|_t \frac{\mathrm{d}T}{\mathrm{d}t} \tag{6?}$$

The use of the partial derivatives presupposes the existence of an $\alpha(t, T)$ function, i.e., it implies that a *unique* α value is determined for any point (t, T) independent of the previous thermal history. Since the point (t, T) can also be approached along an isothermal route, this supposed unique transformed fraction may not deviate from the value calculated isothermally. The following conclusion is therefore inevitable: the alternative formulation implicitly assumes that eqn. (3) in the form of $\mathrm{g}(\alpha) = k[T(t)]t$ remains valid also under non-isothermal conditions. Its time derivative using eqns. (2) and (4b) yields

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \mathrm{f}(\alpha)k(T)\left\{1 + \frac{Et}{RT}2\frac{\mathrm{d}T}{\mathrm{d}t}\right\} \qquad (7?)$$

which modified rate equation can also be derived, e.g., in ref. 4 by rather complicated calculations from eqn. (6?).

This derivation of eqn. (7?) is included here only to illustrate my main point: despite the seemingly sophisticated calculations which are frequently used to derive eqn. (7?) and despite the complicated interpretations also attached to this formalism, its actual meaning, i.e., the transformed fraction which it predicts, is simply as in eqn. (3). The most important feature of this equation $\mathrm{g}(\alpha) = k(T)t$ is evident: a definite value of the transformed fraction is predicted once the actual time, t, and temperature, T, are specified. Some examples have already been published [5] to show that this formalism leads to absurd results. For example, it would predict that treatment of the sample isothermally at a temperature T for a time t results in the same transformed fraction as the path which approximates as closely as we wish to an instantaneous jump to temperature T at time t.

CONCLUSION AND RECOMMENDATION

The fact that the alternative formalism for the description of non-isothermal kinetics is based on the assumption that the transformed fraction is a function only of the actual time and temperature is not properly emphasized by the proponents of this method. It is shown in this note that the solution of their modified rate equation is simply the isothermal expression for the transformed fraction. Since the absurdity of this result is evident in the vast majority of the problems investigated by thermal analysis, it is recommended that before eqn. (6?) or (7?) or any equivalent is used, the basic assumption that the transformed fraction is uniquely determined only by the actual time and temperature be experimentally demonstrated for the given problem.

This "general discussion on non-isothermal kinetics" seems to be a dead end which is prolonged only by a continuous stream of publications which directly or indirectly use a version of eqn. (6?) or apply eqn. (3) under non-isothermal conditions. Once the argument of Felder and Stahel [6] is understood by accepting that the transformed fraction is a path function then the problem is effectively solved: eqn. (1) is to be used as the rate equation (with the necessary caution as is emphasized by Henderson [7]), while the appropriate mathematical approximations of eqn. (5) predict the transformed fraction.

The alternative formalism, eqn. (6?) or the use of eqn. (3) under non-isothermal conditions, is definitely inapplicable to *any* problem, where the transformed fraction is known to depend also on the $T(t)$ path. It is now the responsibility of editorial boards to guard against the re-appearance of the same basic arguments unless some new and convincing experimental and/or theoretical proofs are also offered.

REFERENCES

1 J. Šesták, Thermochim. Acta, 83 (1985) 391.
2 J.H. Flynn and L.A. Wall, J. Res. Natl. Bur. Stand., 70A (1966) 487
3 J.R. MacCallum and J. Tanner, Nature (London), 225 (1970) 1127.
4 A. Dutta and M.E. Ryan, Thermochim. Acta, 33 (1979) 87.
5 L.V. Meisel and P.J. Cote, Acta Metall., 31 (1983) 1053.
6 R.M. Felder and E.P. Stahel, Nature (London), 228 (1970) 1085.
7 D.W. Henderson, J. Thermal Anal., 15 (1979) 325; J. Non-Cryst. Solids, 30 (1979) 301.