Thermochimica Acta, 110 (1987) 95–99
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

REACTION KINETICS IN THERMAL ANALYSIS: A BRIEF SURVEY OF FUNDAMENTAL RESEARCH PROBLEMS

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ABSTRACT

Problems that should be solved for a reliable kinetic treatment of thermoanalytical curves are discussed. The problems are connected with the following topics: the information content of thermoanalytical curves, the evaluation of kinetic parameters, the effect of experimental errors on estimated kinetic parameters and the description of reverse reactions.

INTRODUCTION

Mathematical modelling plays a crucial role in modern science. It helps in understanding the processes being studied, in checking the validity of assumptions and theories and in deducing quantitative conclusions from measured data. In thermal analysis, it is the kinetics of studied reactions under given experimental conditions that could be of help in understanding the reactions fully and in exploring the information content of the measurements. However, even a physically meaningful description of the simplest type of reactions seems to be problematic at present and there is no agreement in the literature [1–4] about the causes of this failure. The aim of this brief survey is to draw attention to a few basic problems that are usually avoided during the kinetic evaluation of thermoanalytical curves.

INFORMATION CONTENT OF A THERMOANALYTICAL CURVE

A basic question with any mathematical description is: how many unknown parameters of the model can be determined from a given data set? If huge data sets are involved, the answer requires sophisticated mathematical methods. However, a single thermoanalytical curve can easily be surveyed by the human eye and in this way it is easy to count how many characteristic

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

0040-6031/87/$03.50

features it has. Even the simplest single-peak (or single-step) thermoanalytical curves have at least three characteristics: the width, the degree of asymmetry and the position on the *T* axis. These characteristics can usually define three independent parameters in the models. It is well worth studying, however, the extent to which a given feature (e.g., the degree of asymmetry) is characteristic of the studied processes. A detailed treatment of these questions was given by Pokol et al. [5].

EFFECT OF EXPERIMENTAL ERRORS ON ESTIMATED KINETIC PARAMETERS

The reliability of estimated parameters is obviously a basic question. In the fortunate fields of scientific research, elegant methods of mathematical statistics can be used, involving confidence intervals, statistical tests, etc. However, the applicability of mathematical statistics depends on the randomness and independence of the errors of the measured data, whereas in the modern thermoanalytical measurements, especially when the data acquisition is computerized, the random components of the experimental errors are negligible. The really significant errors are not random: the actual temperature programmes differ from the prescribed programmes, the baselines are drifted or disturbed by side reactions, the buoyancy of the crucible varies with temperature, etc. The effects of these non-random experimental errors have to be analysed carefully. Although this work has already started (see, e.g., refs. 5 and 6), it is far from complete.

EVALUATION OF A SINGLE THERMOANALYTICAL CURVE

Every kinetic evaluation is based on some comparison between the theory and the experimental data. The various methods of evaluation differ in the type of fit that results. Outside thermal analysis, the standard kinetic evaluation method is the method of least-squares:

$$\sum W_i\left(X_i - X_i^{\text{calc}}\right)^2 = \min \tag{1}$$

where X_i and X_i^{calc} are the measured data and their theoretical counterparts calculated by the solution of the kinetic differential equation(s) and W_i are optional weight factors. In practice, the application of eqn. (1) requires non-linear numerical minimizations carried out by computers.

The method of least-squares can be applied in thermal analysis. The calculations do not require more than a microcomputer with 64 Kbyte of memory [7,8]. The available algorithms can be applied for processes composed of a forward and a reverse reaction [7] and for the evaluation of overlapping thermoanalytical peaks or steps [8].

Nevertheless, kinetic evaluations in thermal analysis are usually based on simple linearizations without considering the fit between the experimental data and their theoretical counterparts. To illustrate the dangers of these procedures, let us consider the kinetic evaluation of a first-order reaction through the following trivial linearization [9]:

$$\ln \frac{\mathrm{d}\alpha/\mathrm{d}t}{1-\alpha} = \ln A - E/RT \tag{2}$$

where α is the molar fraction reacted. The left-hand side of eqn. (2) is a sophisticated transform of the measured data which is not defined at $\mathrm{d}\alpha/\mathrm{d}t = 0$. Simple differentiation shows that the sensitivity of the left-hand side for $\mathrm{d}\alpha/\mathrm{d}t$ is inversely proportional to $\mathrm{d}\alpha/\mathrm{d}t$. In this way, the application of eqn. (2) without special weight factors results in kinetic parameters that are extremely sensitive to the data at the beginning and end of the thermoanalytical curve and having minimal sensitivity to the data in the vicinity of the maximum of $\mathrm{d}\alpha/\mathrm{d}t$. Similar problems also arise in the linearization of the integrated form of the kinetic equations. The uneven sensitivity of the experimental data is not a pure academic problem. It has been reported, for example, that the above types of linearization cannot distinguish between reactions with formal reaction orders of 1, 2/3 and 1/2 [10]. Note that the shapes of the DTG curves of these reactions differ so much from each other that reactions with formal reaction orders of 1, 2/3 and 1/2 can be distinguished by mere visual inspection, without any calculation [11]. Although the uneven sensitivity of the linearizations can be counterbalanced by suitable weight factors [12], it is better to avoid this problem completely by fitting the theoretical α or $\mathrm{d}\alpha/\mathrm{d}t$ data to the measured ones directly.

I do not consider that the least-squares method is the best of the possible methods, but it is a well established way of estimating parameters that can be carried out routinely in the present age of computers with available algorithms. The proposers of other evaluation methods should clearly discuss how and why their methods give results that are better than or equivalent to those given by the standard least-squares method.

EVALUATION FROM MORE THAN ONE THERMOANALYTICAL CURVE

A single thermoanalytical curve is not always suitable for discrimination between different kinetic models [3] and defines only a limited number of unknown parameters. Hence it is reasonable to base the kinetic studies on several measurements, including measurements at different heating rates and/or isothermal measurements. If the applied kinetic model is not a single equation with three or less unknown parameters, the measured curves have to be evaluated together. This is a well-known and well-established procedure in thermal analysis. Nevertheless, there are (at least) two problems of general importance here that deserve further consideration:

(i) Important factors such as the sample geometry, thermal contact between the sample and the sample holder and the number of lattice defects, weak links and impurities may vary from measurement to measurement (especially if small samples are used to avoid mass and heat transfer problems) and it is not yet clear how these differences should be handled during the evaluation.

(ii) The different heating rates or the different temperatures of isothermal measurements may lead to different importances of the transport processes, reverse reactions and side reactions. It is an open question what one should do in such cases.

REVERSE REACTIONS

The concentration of volatile products in the ambient gas near to the surface of the sample and inside the pores of the sample is a crucial problem in thermal analysis at atmospheric pressure [2]. At present, the magnitude of this concentration seems to be known only in specially designed experiments. The effect of this concentration is usually connected with the difference between the actual pressure of the volatile product and the equilibrium pressure of the decomposition [2,7,13,14]. There is an open question here: what type of equilibrium pressure can be connected meaningfully with a decomposing sample? Let us consider a simple reaction

$$A_{\text{solid}} = B_{\text{solid}} + C_{\text{gas}} \tag{3}$$

Even the simplest reactions of this type are composed of several elementary processes, including some sort of nucleation, the propagation of the reaction in certain domains or surfaces, the collapse of the original crystal or amorphous structure when the concentration of A decreases below some critical value in a given domain and the rearrangement into the crystal or amorphous structure of B when the reaction is complete in a domain. The theoretical definition of the equilibrium pressure refers to the pure phases of A, B and C and does not have any connection with the nascent ions or molecules of B in a crystal structure of A or with the intermediate states between A and B. In this way the molecules of the volatile products may hinder the decomposition by reacting again with the nascent nuclei of B even if the overall decomposition is not reversible or is far from equilibrium [15]. This type of reasoning would lead to a simpler explanation of the observed deviations from published theories than the assumption of special chemisorption phenomena [16,17].

SOPHISTICATED MATHEMATICAL MODELS

Most of the processes studied by thermal analysis should be described by complex mathematical models composed of more than one equation and containing many unknown parameters. However, the elaboration and use of such models can hardly be successful without solving the problems of the kinetic description of the simple reactions under the experimental conditions used in thermal analysis. At present, studies connected with the kinetic evaluation of thermoanalytical curves can be regarded as the production of building blocks for a really useful mathematical background to thermal analysis.

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