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On the controversies in TA kinetics

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Abstract

A critical assessment of the usual linearizing methods of kinetic evaluation of TA data is given. The proposal is to abandon the "classical" methods and to apply complex non-linear optimization with the permanent inclusion of all participated differential equations (overall evaluation) which could end the confusion in the results of TA kinetics.

ON THE SITUATION OF TA KINETICS

In the last decades TA has been developed to a high degree of technical maturity, and equipment has become available that was not originally designed for kinetic investigations but for the technical characterization of materials and processes under non-isothermal temperature programs. This situation has largely remained unchanged.

Most investigations by this technique are restricted to solid state materials. Liquids and solutions are usually investigated by other techniques.

However, the solid state does not possess homogeneity of thermal and compositional conditions. In all solid-state processes or reactions this causes some difficulties for the quantitative evaluation of the experiment [1,2]. Therefore, temperature and enthalpy calibrations have been used, with increasing success.

Because there is no possibility of permanently mixing the sample, the only solution was the diminution of the sample, which was followed by a miniaturization of the equipment. Nevertheless there remains the contradiction between real reaction and the expected model behaviour on the basis of a mathematical equation. An additional difficulty is that simple reactions are the exception whereas two- or more-step reactions/processes are the rule.

Computer-aided experiments provide an enormous quantity of data, whose accuracy and reproducibility are definitely increasing. But it is

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

grossly misleading to deal with these data as if they refer to simple reactions/processes. This would be the mathematical solution of an "as if" situation. Still more remarkable is the circumstance that many investigators let the black box become rather independent and their mathematical solutions are forced ones: this has led to a spate of publications on this subject, i.e. an insufficiently founded desire for a kinetic handling of data has spread.

The responses to this situation are manifold, ranging from complete rejection and anathematization of TA kinetics to a rational assessment of the scientific limits of TA kinetics today. Remarkable papers and lectures have been given at ESTAC-4/Jena 1987 [3,4] and ESTAC-5/Nice 1991 [1,2].

THE MAIN FEATURES OF TODAY'S TA KINETICS

(1) There are some exact formulae, e.g. that of Borchardt–Daniels [5] and, in addition, many approximations with very different simplifications.

(2) Nearly all work is done with linearizing graphics by skillful choice of coordinates irrespective of the uncertainties produced by this.

(3) Only part of the measured data are included, sometimes only one point, e.g. the maximum.

(4) Exact evaluation methods are given for simple (one-step) reactions. The methods for complex reactions can be compared with estimations.

(5) Any TA technique is exclusively suitable for one property, e.g. mass, ΔT or enthalpies. If in the case of DSC the process enthalpies for two separate steps are very different, then the lower energy step is more difficult to evaluate than the higher one, even if the reaction with the smaller ΔH is rate-determined. However, it is a prerequisite of the method that the changes of concentration and enthalpy be proportional.

THE OPINION OF THE AUTHOR

(1) The measured data reflect facts and should be interpreted theoretically as far as possible.

(2) The degree of interpretation depends on the background information about the considered process. But more light should be thrown into the "black boxes".

(3) We have to answer the same questions as those posed in other fields of kinetics:

(3.1) What is the reproducibility and accuracy of the data sets?

(3.2) What kinds of processes are expected?
- —physical: transformation, nuclear formation or growth, diffusion, melting, etc.
- —chemical: one-step or two-step reaction
- —combination of both

(3.3) What intermediates and final products were detected?
(3.4) What mechanism can be proposed for the rate-determining reaction?
(3.5) What differential equation or system of equations can be taken into consideration?

(4) Moreover, a mathematical fitting to the experimental curve may be helpful if this is advantageous for practical purposes, e.g. for quantitative comparisons in an industrial laboratory where the experimental conditions are of the same kind. Applying the well-known kinetic equations for determining the parameters, we should avoid the terms activation energy, frequency factor and reaction order, adopting instead the terms proposed by the author in 1987 [3].

WHAT ARE THE MAIN DEMANDS?

(1) Experiments should be performed under optimal conditions with highest accuracy. The prerequisites for the application of the model equations should be fulfilled as far as possible. The conditions must be such that the inhomogeneity of the temperature distribution in the sample can be neglected and the heterogeneity of the composition is low, e.g. single crystals are frequently more unfavourable than the same amount of polycrystalline material.

(2) Kinetic evaluation should be done using methods which yield the largest measure of statistical security for the calculated parameters.

Only if both demands are met can we solve our problems.

WHAT DO WE EXPECT FROM THE EVALUATION METHOD?

(1) It must include the total data set in the calculation.

(2) For the determination of the parameters E, k_0 and n, an error for one of these is not allowed to influence directly the magnitude of the other. This gives rise to the so-called compensation effect.

(3) Because complex reactions are "normal" cases, it must be possible to make an optimized evaluation of two- and three-step reaction models as well as for parallel and consecutive reactions. This must be done according to the corresponding system of differential equations for the expected or possible mechanism. The evaluation must include the variation of those models which appeared to be possible on the basis of all our knowledge of the given process. A "black box" method is unacceptable.

(4) For the evaluation, all data should be simultaneously processed by the computer.

The author's proposal is to abandon the "classical methods". The best of them [5,6] might be used to estimate parameters in the following procedure.

> The only way to derive a satisfactory set of parameters from well conducted experiments is non-linear optimization, with the permanent inclusion of all the differential equations describing the processes involved. One variant of this procedure was given by Opfermann et al. in Jena [7]. Another variant which needs less computing time was developed in Greifswald by Mentel and Anderson [8].

In this procedure, data sets from several experiments at different heating rates are required. The higher the quality of the experiments, the fewer the heating rates needed. Employing a modern PC (286-486), the evaluation can be done directly at the TA equipment. The recommended programs offer a high level of user comfort but should be further improved. Suitably estimated values of the parameters at the start, shorten substantially the expense of computing time. For the estimation of E, k_0 and n, we demand the application of the best classical linearizing methods which are free of approximations [5,6]. This is achieved in the first part of the program. Thereafter, non-linear optimization begins, using a complex program that produces one or more sets of statistically secured activation parameters E_i, k_{0i}, n_i. A modified F-test records the optimal adaptation of the data to the considered reaction model. The evaluation is finished by a graphical comparison of the experiment and the calculated model on the monitor.

In practice, these results are far reaching. By means of optimized parameters the real behaviour under changed conditions is given by simulation. In this way the reaction course under technologically desirable terms, e.g. as temperature profiles and compositions, can be predicted provided scale transformation is allowed.

Finally we can state that the problems of complex reaction kinetics in TA can only be solved in a closed calculation procedure with the inclusion of all the differential equations involved. The improved experimental equipment can then be used to reach the next level in TA kinetics.

But the best way to achieve optimized parameters is to make comparisons with methods other than TA.

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