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ON THE KINETIC EVALUATION OF THE THERMOGRAVIMETRIC CURVES

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ABSTRACT

The information content of the non-isothermal TG curves is discussed. At simple surface reactions, three formal characteristics of the measured curves (the width, the asymmetry and the position on the temperature axis) define uniquely three kinetic parameters: the activation energy, the formal reaction order and the preexponential factor. The actual determination of these kinetic parameters should be based on the least squares fitting of the solution of the kinetic differential equation to the experimental data. To illustrate it, the dehydratation of calcium oxalate monohydrate is treated.

INTRODUCTION

For the exploitation of the information content of the thermoanalytical measurements, some sort of quantitative mathematica description is needed. For the majority of the processes studied by thermal analysis, complex mathematical models with many parameters would be necessary. At present, however, there are controversies even at the description of the simplest type of reactions by equations of form

$$dx/dt = A\ e^{-E/RT}\ f(x) \qquad (1)$$

where x is the reacted mole fraction and f(x) is a function. It has been shown [1] that mathematically different forms of f(x) can result in the same thermoanalytical curves at linear heating programs. Hence some information on f(x) has to be obtained from other sources, e.g. from theoretical considerations or from isothermal measurements. Having chosen the proper form of f(x), the evaluation of the non-isothermal measurements has better defined goals: the determination of a few kinetic parameters and the study of their variation (or constancy) under different experimental conditions. If f(x) can be approximated formally by a function proportional to $(1-x)^n$, the kinetic parameters are E, n and A. There are critical opinions, however, claiming that the information content of a thermoanalytical curve is not sufficient even for the

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estimation of two unknown parameters, A and E [2]. In our opinion as it has been outlined in ref.[3], the three kinetic parameters are uniquely defined by three independent geometric characteristics of the thermoanalytical curves: the width, the asymmetry and the position on the T axis. These considerations are plausible for the peaks of the differential type curves, but it has to be proven that the asymmetry of the thermogravimetric curves is a well defined property as well. In the present paper we shall discuss this problem and show examples that the correct evaluation of the TG curves can surely give three kinetic parameters.

EXPERIMENTAL

The dehydratation of calcium oxalate monohydrate was studied since it seemed to be a sufficiently simple, well defined and well known reaction for kinetic test calculations. The calcium oxalate monohydrate was an analytically pure powder distributed by company MO' for thermoanalytical purposes. The measurements were made by a Perkin-Elmer TGS-2 thermobalance. The data were collected, stored and evaluated by a PDP-11/34 computer. 25 TG curves were measured. The initial sample mass varied between 50 μg and 7 mg. The atmosphere was argon. A few measurements were carried out in helium. Various flow rates were set between 100 and 270 ml/min. The applied heating rates were 4, 10, 20 and 60 K/min.

THE SHAPE OF THE TG CURVES

The usual definitions of the various "shape indices" are based on dx/dt data or require the knowledge of the position of the highest dx/dt value and in this way they involve the uncertainty of the differentiation of the TG data. It is possible, however, to define shape indices without the differentiation of the TG curves. Let us regard, for example, the following quantity:

$$\frac{1/T_{0.7} - 1/T_{0.9}}{1/T_{0.1} - 1/T_{0.3}} \qquad (2)$$

where the temperatures $T_{0.1}$, $T_{0.3}$, $T_{0.7}$, and $T_{0.9}$ belong to $x = 0.1, 0.3, 0.7$ and 0.9, respectively. From a mathematical point of view, formula (2) uniquely defines the value of the formal reaction order, n [4]. From a physical point of view, formula (2) is equal to one at symmetric curves and its deviation from the unity measures the asymmetry of the TG curves. Hence formula (2) defines a "shape index".

We do not recommend, however, the application of formula (2)for actual kinetic evaluations. The significance of the various shape indices is theoretical: they may help to study the information content of the measurements and the effects of those systematic errors which distort the shape of the thermoanalytical curves [4]. In actual kinetic calculations the shape indices prove to be too sensitive to the random components of the experimental errors since they use only a few of the measured points.

KINETIC EVALUATION BY LEAST SQUARES CURVE FITTING

Though it is possible to develop more sophisticated shape indices which use all measured data, there is no real need for it. Instead of such work, the method of least squares should be used: the solution of eqn. (1), denoted by $x^{calc}(t)$, should be fitted to the experimental data by finding the minimum of

$$\sum \left[x^{calc}(t_i) - x^{obs}(t_i)\right]^2 \qquad (3)$$

The minimization can be made numerically. Though the numerical methods used in the isothermal reaction kinetics fail frequently in non-isothermal calculations, the various convergence problems can easily be eliminated by proper parameter transformations [5]. When the least squares method results in a good fit, $x^{calc}(t)$ also approximates the geometric characteristics of the measured curve well and in this way the least squares method utilizes the information content of the shape of the TG curve well. If $x^{calc}(t)$ proves to be a bad approximation of $x^{obs}(t)$, then eqn. (1) is inadequate for the description of the measurements and other forms of f(x) or other type of kinetic equations are needed(instead of trying the evaluation by shape indices or by other methods).

THE KINETICS OF THE DEHYDRATATION OF CALCIUM OXALATE MONOHYDRATE

The dehydratation of $CaC_2O_4.H_2O$ strongly depends on the experimental conditions [6,7]. In our opinion, it is more or less a diffusion controlled surface reaction. The reaction surface can only approximately be defined and it has obviously an irregular geometry. Hence any f(x) function is only a formal approximation of the reaction surface in this case. We applied $f(x) \cong (1-x)^n$, which is the usual eqn. for surface reactions. 25 measurements were made under various experimental conditions described in the experimental section. The curves were evaluated by the method of least squares. Good fit was achieved at every measurement. The deviation between the observed and the calculated curves was about 0.25 % at initial masses higher than 1 mg and about 0.5 % in the other cases. The kinetic parameters have shown the usual systematic dependence on the experimental conditions [6,7]. The factors increasing the diffusion control have decreased the activation energy. The activation energy varied between 64 and 104 kJ/mol, which agrees well with the range determined by other type of evaluation by Manche and Carrol [8]. The logarithm of the preexponential factor varied parallel with the activation energy, its values were between 6 and 12. The formal reaction order varied between 0.4 and 0.7, indicating that the geometry of the surface where the reaction can proceed depends on the experimental conditions. At fixed experimental conditions, however, the measurements gave essentially the same results with sufficiently small deviations. Thus the standard deviations calculated from groups of four repeated measurements were about 0.02 - 0.05 for n, 2 - 3 kJ/mol for E and about 0.3 for log A.

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