Journal of Thermal Analysis, Vol. 34 (1988) 761–767.

UTILIZATION OF CRITERIAL EQUATIONS FOR QUANTITATIVE PROCESSING OF THERMOGRAVIMETRIC RESULTS

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(Received April 27, 1987)

A system of criterial equations is proposed for determining the parameters of kinetic equations by thermogravimetric results. The criterial equations take into account the particularities of the effect of each parameter on the shape and position of the TG curve. It is shown that the method ensures uniqueness of the solution obtained, which best fits to the experimental data.

Although TG is widely used to study the kinetics of solid-phase reactions, reports of various authors cannot always be considered as reliable.

The factors affecting the quality of mathematical description of processes taking place under non-isothermal conditions may be divided into two major groups: those connected with the authenticity of the experimental procedure, and those related to the selection of the method for quantitative description of TG results.

In this paper we do not deal with the authenticity of the experiments, and assume that the experimental data are reliable, i.e. the temperature recorded is equal to the temperature of the sample studied (and the temperature is constant in the whole sample), and that the distortions of mass loss caused by apparatus and other noises can be neglected. About the details of the procedure regarding the above requirements see [3, 5].

For the mathematical description of chemical processes taking place in solid phase, the equation of formal kinetics is utilized most frequently, assuming that the temperature dependence of the rate of reaction follows the Arrhenius law:

$$d\alpha/dt = Z\exp(-E/RT)(1-\alpha)^n \tag{1}$$

or for the case of uniform temperature increase:

$$d\alpha/dT = (Z/q)\exp(-E/RT)(1-\alpha)^n \tag{2}$$

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where α is the degree of conversion of the substance, t is time, T is temperature, q is heating rate, Z is the preexponential factor, E is the activation energy and n is the order of the reaction.

Usually the solution of the reverse task of chemical kinetics is based on linearizing Eq. (2) with respect to kinetic parameters by means of various transformations and assumptions, and the kinetic parameter of interest is found by linear least squares method (LSM). This approach does not require cumbersome calculations, but it may, however, result in constants that are shifted relative to their true values, which leads to discrepancy between experimental data and theoretical values.

This can be avoided by applying non-linear computerized numerical calculation, discussed in detail in [4].

For the critical function to be minimized, a quantity is used numerically characterizing the degree of coincidence of experimental and theoretical data.

In the followings, we shall understand by the quantity the standard deviation (SK) assuming the value "0" at full coincidence and "1" at full non-coincidence of calculated and experimental curves.

The major drawbacks of this approach, related to the following properties of the criterial function (SK) are discussed in [4]. Firstly, it has the shape of a flat pit, the presence of which is explained by the compensation effect, which is actually a close correlation between parameters E and Z. Secondly, the criterial function has a plateau (cf. Fig. 2), causing difficulties in selecting the initial approach. Thirdly, some disagreement always occurs between the quantitative description and the true behaviour of the system that may lead to local minima of the criterial function comparable in value with the global minimum.

Taking into account of all these particularities of the criterial function a great amount of calculations is required to solve the problem.

The aim of this work was to develop a method for finding kinetic parameters ensuring that reliable results can be obtained only by performing relatively small amount of calculations.

The essence of the novel approach is the following: instead of searching for the minimum of the SK function within the total range of the parameters, the successive solution of criterial functions is applied, these functions take into account of the particular effect of each parameter on the shape of the curve described by Eq. (2). For example, in the literature it has been noted frequently that the presence of the compensation effect, raising difficulties in non-linear computerized numerical calculations, may sharply reduce the range in which optimum values of E and Z should be sought, since this effect demonstrates their close relationship. Making use of the relationships between E and Z in their explicit [8, 6] or implicit [7] form allows to reduce the amount of calculations substantially, since it, in fact, reduces the optimization task.

In the suggested method we take into account that changing Z (as follows from the integral form of Eq. (2)) results in a proportional change of the $g(\alpha)$ value:

$$g(\alpha) = Z\int \exp(-E/RT)$$

$$n=1 \quad g(\alpha) = -\ln(1-\alpha)$$

$$n\neq 1 \quad g(\alpha) = 1/((1-n)\cdot(1-(1- =a)^{1-n}))$$

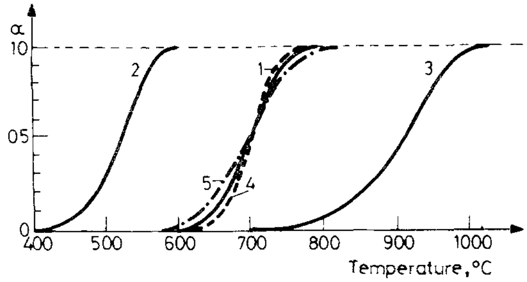

Fig. 1 Curves obtained with the criterial Eq. (2) for $n=1$; 1 – E = 209.5 kJ/mol, $Z = 0.1\cdot 10^{11}$; 2 – E = 209.5 kJ/mol, $Z = 0.1\cdot 10^{13}$; 3 – E = 209.5 kJ/mol, $Z = 0.1\cdot 10^{9}$; 4, 5 – Satisfy the conditions $FZ = 0$ at E = 168 kJ/mol and 251 kJ/mol, resp.

expressed by the shift of the curve along the temperature axis (cf. Fig. 1). The value of the shift can be characterized by the difference (FZ) between the temperature of the calculated and experimental curves at that degree of transformation where the inflexion point of the experimental curve is:

$$FZ = T^{\mathrm{exp}}_{(\alpha=\alpha_s)} - T^{\mathrm{cd}}_{(\alpha=\alpha_s)} \qquad (3)$$

where *exp* and *cd* are indices for experimental and calculated values, resp., and s is an index characterizing the inflexion point.

Why the inflexion point was chosen as a characteristic point is discussed below.

Derivation of Eq. (2) and putting it equal to zero in the inflexion point gives

$$n(-d\alpha/dT)+(E/RT_s^2)(1-\alpha_s) = 0$$

It follows from the above that if the condition that $FZ = 0$ is satisfied and the value of n is fixed, changes in parameter E lead to the proportional changes of $d\alpha/dT$, that manifest itself in the turn of the calculated curve to the inflexion point (cf. Fig. 1). Therefore, as criterion accounting for the effect of parameter E (at fixed n) on the position of the calculated curve, evaluating the correctness of the calculated values

E and Z, the sum of differences in temperature may serve, the different values on the two sides of the inflexion point of the experimental curve being considered with different signs:

$$FE = \sum_{i=1}^{s} (T^{\mathrm{exp}}_{(\alpha=\alpha_i^{\mathrm{exp}})} - T^{\mathrm{cd}}_{(\alpha=\alpha_i^{\mathrm{exp}})}) - \sum_{i=s}^{N} (T^{\mathrm{exp}}_{(\alpha=\alpha_i^{\mathrm{exp}})}) - T^{\mathrm{cd}}_{(\alpha=\alpha_i^{\mathrm{exp}})}) \quad (4)$$

where i is the number of the vector elements used in the calculation of the experimental data, and N is the number of experimental points used.

The value of parameter n affects the position of the inflexion point on the curve described by Eq. (2), utilized for the estimation of this parameter [9], and it has been shown that the inflexion point on the calculated curve is shifted when n changes.

If the condition

$$F(E, n, Z, FZ = 0) = 0$$

is satisfied, then the calculated curve intersects the experimental curve in the inflexion point, but does not coincide with it, and the more the value of n differs from the true value, the more the slope of the curve against the ordinate axis in the point ($\alpha = \alpha_s$) changes; consequently, as a criterion for the correctness of the calculated value of the parameter, the value FN (cf. Fig. 1) may be accepted:

$$FN = (\mathrm{d}\alpha/\mathrm{d}T)^{\mathrm{cd}}_{(\alpha=\alpha_s)} - (\mathrm{d}\alpha/\mathrm{d}T)^{\mathrm{exp}}_{(\alpha=\alpha_s)} \quad (5)$$

In this way the values of the kinetic parameters can be found by solving the equation

$$FN(n, E, Z, FE = 0, FZ = 0) = 0 \quad (6)$$

Analysis of the criterial equations demonstrated that all three criterial functions change monotonously (cf. Figs 2, 3, 4), and consequently Eq. (6) has a unique solution.

In order to find the roots of each criterial equation, a traditional method (e.g. the "intersecting" method) can be used.

To test the applicabilty of the method, a computerized experiment was carried out. The results of the numerical integration of Eq. (2), with $E = 209.6$ kJ/mol, $Z = 0.1 \cdot 10^{11}$, $n = 1$ were taken for experimental data. The roots of Eqs (3), (4) and (5) were determined so as to obtain the required accuracy by each of the criteria. To achieve that the error in the determination of the kinetic parameters shall not exceed 0.1%, the values of the criteria must not differ from "0" by more than 0.1 for the criterion FE, 0.01 for the criterion FZ and 0.001 for the criterion FN.

To reach such accuracy in the determination of the roots of each of the criterial equations, the number of returns to the calculation of the criterion values is 3–4. The total number of such returns in the solution of this task was 36. The calculated values of the kinetic parameters were $E = 208.9$ kJ/mol, $Z = 0.934 \cdot 10^{10}$, $n = 1.01$.

To determine kinetic parameter values with similar accuracy by means of non-linear computerized numerical calculation (using the simplex method), the number of returns to the calculation of the target function was 485.

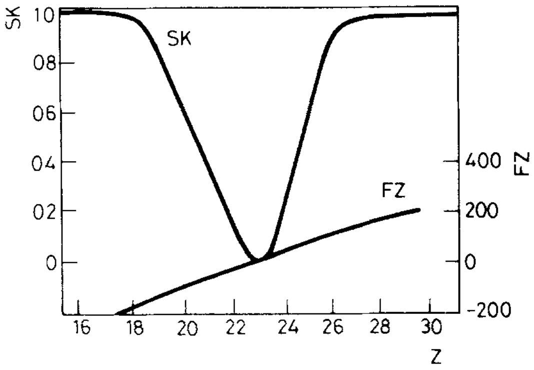

Fig. 2 Relationships of the criteria *SK* and *FZ* vs. *Z*

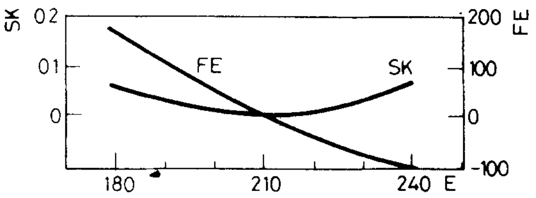

Fig. 3 Relationships of the criteria *SK* and *FE* vs. *E* at satisfaction of the condition *FZ* = 0

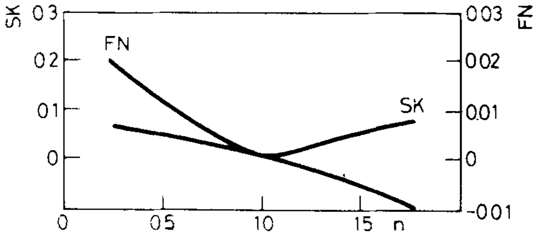

Fig. 4 Relationships of the criteria *SK* and *FN* vs. *n* at satisfaction of the condition *FE* (*FZ* = 0) = 0

Thus, the approach proposed allowed us to reduce the amount of calculations by more than an order of magnitude, simultaneously maintaining the accuracy of determination of the kinetic parameters.

The standard deviation calculated for the found values of the parameters serves as usual, as a criterion to what extent the mathematical description corresponds to experimental data.

The criterial functions *FZ*, *FE*, *FN* are such that their "0" value corresponds to the minimum range of the function *SK* (cf. Figs 2, 3, 4). Therefore the set of kinetic parameters which is optimal from the viewpoint of this criterion corresponds to the solution of Eq. (6).

The fulfilment of condition (6) indicates that the calculated curve (i) intersects the experimental curve in the inflexion point of the latter, (ii) it coincides with the experimental curve in the range of the inflexion point, and (iii) the sum of discordances of the curves regarding temperature is minimal on both sides of the inflexion point.

Let us now turn to the question why the inflexion point was taken as basis. The following consideration led us in this choice: first, the inflexion point characterizes the range in which the transformation rate is maximum and the shape of this section of the curve is most sensitive to changes of the parameters E and Z; it is known, for example, that the value n practically does not effect the shape of the initial section of the TG curve, this fact being utilized for the evaluation of E when the mechanism of the process to be studied is unknown [10]. Second, the initial and final section of the experimental curve are usually distorted, owing to factors not accounted for in the mathematical model (Eq. (2)).

In order to check the efficiency of the suggested method for determining the activation parameters of actual processes, quantitative processing of the thermoanalytical curves of calcium oxalate obtained at different heating rates was carried out. The thermoanalytical curves were recorded using a Setaram THU 2000 with B–70 balance. Recording conditions were the following: measuring cell: platinum plates, air atmosphere, sample mass 0.18–0.20 g.

The results of processing the data obtained by the suggested method and by non-linear computerized numerical calculation are listed in Table 1.

The data in the Table indicate that the described method for quantitative processing of TG results, based on the utilization of the particular effect of each kinetic parameter on the shape of the TG curve ensures uniqueness of the solution obtained, independently of the choice of the initial approach, and allows to evaluate the kinetic parameters with an accuracy not less than obtained with non-linear computerized numerical calculations, but at a substantially lesser amount of the necessary calculations.

Table 1 Quantitative processing of TG curves obtained with calcium oxalate at different heating rates q

q, deg/min	Processing with the criterial equation method				Processing with non-linear computerized numerical calculation			
	n	E, kJ/mol	$\ln Z$	SK	n	E, kJ/mol	$\ln Z$	SK
0.503	0.98	400	66.8	0.0082	0.99	407	68.2	0.0076
0.720	1.00	403	67.6	0.0150	1.02	409	67.8	0.0142
1.085	0.96	388	65.0	0.0105	0.98	394	66.4	0.0096
2.067	1.04	410	67.6	0.0138	1.04	415	69.8	0.0120
3.250	0.98	400	67.2	0.0073	1.01	411	69.2	0.0052
Mean value	0.99	400	66.8	0.0129	1.01	407	68.2	0.0097

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Zusammenfassung — Zur Bestimmung der Parameter kinetischer Gleichungen mittels thermogravimetrischer Ergebnisse wurde ein System charakteristischer Gleichungen vorgeschlagen. Dieses zieht die Besonderheiten der Effekte jedes einzelnen Parameters auf Lage und Verlauf der TG-Einzelheiten in Betracht. Es wird gezeigt, daß durch das Verfahren die bestmöglichste Lösung erhalten wird, welche mit den experimentellen Daten am besten übereinstimmt.

Резюме — Для определения параметров кинетического уравнения по результатам ТГ-анализа предложено использовать систему критериальных уравнений, которые учитывают особенности влияния каждого из параметров на вид и положение ТГ-зависимости. Показано, что используемый метод гарантирует единственность получаемого решения, которое наилучшим образом описывает экспериментальные данные.