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THE NON-LINEAR LEAST SQUARES METHOD IN NON-ISOTHERMAL KINETICS

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ABSTRACT

The non-isothermal least squares method for the evaluation of the kinetic parameters was generalized to non-isothermal kinetics of heterogeneous reactions.

INTRODUCTION

The kinetics of decomposition of solids is often formally described in the terms of the reaction order model[1]. As shown by Norris et al.[2], due to the non-linear appearance of the reaction order, n, in the rate equations, it is difficult to evaluate the kinetic parameters to whom different reliabilities are conferred, according to the method used for linearization.

In this paper we try to generalize the non-linear least squares method, applied by Judd and Norris[3], for the evaluation of kinetic parameters from isothermal data, to non-isothermal kinetics.

1. GENERALITIES

Let us consider the functional relationship:

$$\varphi = f(x_1, x_2, ..., x_n, p_1, p_2, ..., p_m) \tag{1}$$

where the values of φ, as well as those of the variables x_1, x_2, ..., x_n, can be measured and $p_1, p_2, ..., p_m$, represent a set of parameters.

The problem is to determine the best values of the set of parameters, $p_1, p_2, ..., p_m$, the function f being known.

For simplicity sake, we shall introduce the following notations:

$$X_i = (x_1^i, x_2^i, ..., x_n^i) \tag{2}$$

$$P = (p_1, p_2, ..., p_m) \tag{3}$$

where the subscript i on the left-hand side, as well as the same superscript on the right-hand side of the relationship (2), indicate particular values of the variables $x_1, x_2, \ldots, x_n$. The deviation r_i of the function $f(X_i, P)$ with respect to the measured one, φ_i, can be defined as:

$$r_i = f(X_i, P) - \varphi_i \tag{4}$$

As we do not know the true value of P, but an approximate one, $P^{(n)}$, the approximation of the deviation r_i will be given by:

$$R_i = f[X_i, P^{(n)}] - \varphi_i \tag{5}$$

where $P^{(n)}$, $(n = 0, 1, 2, \ldots)$ are successive approximations of the parameters P.

By expanding the function $f(X_i, P)$ in a truncated Taylor series about the parameters $P^{(n)}$, we get:

$$f(X_i, P) = f[X_i, P^{(n)}] + \sum_{i=1}^{m} \frac{\partial f}{\partial p_i^{(n)}} \Delta p_i^{(n)} \tag{6}$$

$$r_i = R_i + \sum_{i=1}^{m} \frac{\partial f}{\partial p_i^{(n)}} \Delta p_i^{(n)} \tag{7}$$

where $\Delta p_i^{(n)}$ is the largest absolute uncertainty corresponding to the nth order approximation of the p_i value.

According to the theory of the least squares, the most probable values of the parameters p_i are those for which the expression:

$$Q = \sum_{i=1}^{N} r_i^2 \tag{8}$$

is at a minimum, N being the number of experimental points. Taking into account relationships (4) and (8), this condition can be written as:

$$\frac{\partial Q}{\partial p_j^{(n)}} = 2 \sum_{i=1}^{N} r_i \frac{\partial f_i}{\partial p_j^{(n)}} = 0 \tag{9}$$

From equations (9) and (7), it follows that:

$$\sum_{i=1}^{N} \left[R_i + \sum_{k=1}^{m} \frac{\partial f_i}{\partial p_k^{(n)}} \Delta p_k^{(n)} \right] \frac{\partial f_i}{\partial p_j^{(n)}} = 0$$

$$\sum_{i=1}^{N} R_i \frac{\partial f_i}{\partial p_j^{(n)}} + \sum_{k=1}^{m} \left[\sum_{i=1}^{N} \frac{\partial f_i}{\partial p_j^{(n)}} \frac{\partial f_i}{\partial p_k^{(n)}} \right] \Delta p_k^{(n)} = 0 \tag{10}$$

For $j = 1, 2, \ldots, m$

and

$k = 1, 2, \ldots, m$

we obtain a system of m equations in the m unknowns $\Delta p_k^{(n)}$ (normal equations) whose matrix form is:

$$\begin{bmatrix} \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_1}\cdot\frac{\partial f_i}{\partial p_1} & \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_1}\cdot\frac{\partial f_i}{\partial p_2} & \cdots & \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_1}\cdot\frac{\partial f_i}{\partial p_k} & \cdots & \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_1}\cdot\frac{\partial f_i}{\partial p_m} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_j}\cdot\frac{\partial f_i}{\partial p_1} & \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_j}\cdot\frac{\partial f_i}{\partial p_2} & \cdots & \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_j}\cdot\frac{\partial f_i}{\partial p_k} & \cdots & \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_j}\cdot\frac{\partial f_i}{\partial p_m} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_m}\cdot\frac{\partial f_i}{\partial p_1} & \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_m}\cdot\frac{\partial f_i}{\partial p_2} & \cdots & \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_m}\cdot\frac{\partial f_i}{\partial p_k} & \cdots & \sum_{i=1}^{N}\frac{\partial f_i}{\partial p_m}\cdot\frac{\partial f_i}{\partial p_m} \end{bmatrix} \times \begin{bmatrix} \Delta p_1 \\ \Delta p_2 \\ \cdots \\ \Delta p_k \\ \cdots \\ \Delta p_m \end{bmatrix} =$$

$$= -\begin{bmatrix} \sum_{i=1}^{N} R_i \frac{\partial f_i}{\partial p_1} \\ \cdots\cdots \\ \sum_{i=1}^{N} R_i \frac{\partial f_i}{\partial p_j} \\ \cdots\cdots \\ \sum_{i=1}^{N} R_i \frac{\partial f_i}{\partial p_m} \end{bmatrix} \tag{11}$$

where

$$\frac{\partial f_i}{\partial p_j} = \frac{\partial f[X_i, P^{(n)}]}{\partial p_j^{(n)}}$$

Introducing the notations:

$$\sum_{i=1}^{N} \frac{\partial f_i}{\partial p_j}\frac{\partial f_i}{\partial p_k} = \mathrm{DJ.DK}$$

$$\sum_{i=1}^{N} R_i \frac{\partial f_i}{\partial p_j} = \mathrm{CJ}, \tag{12}$$

the system (11) can be written as:

$$\begin{bmatrix} \mathrm{D1.D1} & \mathrm{D1.D2} & \ldots & \mathrm{D1.DK} & \ldots & \mathrm{D1.DM} \\ & \cdots & & \cdots & & \\ \mathrm{DJ.D1} & \mathrm{DJ.D2} & \ldots & \mathrm{DJ.DK} & \ldots & \mathrm{DJ.DM} \\ & \cdots & & \cdots & & \\ \mathrm{DM.D1} & \mathrm{DM.D2} & \ldots & \mathrm{DM.DK} & \ldots & \mathrm{DM.DM} \end{bmatrix} \times \begin{bmatrix} p_i \\ \\ p_k \\ \\ p_m \end{bmatrix} = -\begin{bmatrix} \mathrm{C1} \\ \\ \mathrm{CJ} \\ \\ \mathrm{CM} \end{bmatrix} \tag{13}$$

By solving this system, we get:

$$p_j^{(n+1)} = p_j^{(n)} + \Delta p_j^{(n)}, j = 1, 2, \ldots, m$$

Taking into account this last result, the best values of the parameters P can be obtained by starting with an initial approximation $p_j^{(o)}$ and improving it until $\Delta p_j^{(n)} < \varepsilon_j$, where ε_j is the admitted absolute incertainty for the measurement of the parameter p_j.

2. VARIANT OF THE NON-LINEAR LEAST SQUARES METHOD FOR NON-ISOTHERMAL KINETICS

If we cannot directly measure the φ values, the non-linear least squares technique can still be applied. To demonstrate this statement, let us consider a quantity ψ which cannot be directly measured but can be calculated from the experimental data, using the functional relationship:

$$\psi = \mathrm{f}(X, P) \tag{14}$$

As the X_i values can be directly measured, due to experimental errors, they are shifted from the true ones, X_{t_i}, i.e.:

$$\mathrm{f}(X_{t_i}, P) \neq \mathrm{f}(X_i, P) = \psi_i$$

Under such conditions, the deviations r_i and its approximation R_i can be defined as follows:

$$r_i = \mathrm{f}(X_i, P) - \mathrm{f}(X_{t_i}, P) \tag{15}$$

$$R_i = \mathrm{f}[X_i, P^{(s)}] - \mathrm{f}(X_{t_i}, P) \tag{16}$$

By choosing the function f so that $\mathrm{f}(X_t, P) = 0$ and taking into account relationships (15) and (16), we get:

$$r_i = R_i + \sum_{j=1}^{m} \frac{\partial \mathrm{f}}{\partial p_j^{(s)}} \Delta p_j^{(s)} = \mathrm{f}[X_i, P^{(s)}] + \sum_{j=1}^{m} \frac{\partial \mathrm{f}}{\partial p_j^{(s)}} \Delta p_j^{(s)} \tag{17}$$

which is analogous to eqn (7). Thus, the results mentioned in former section are still valid if one changes the approximations R_i into $\mathrm{f}[X_i, P^{(s)}]$.

3. THE APPLICATION OF THE NON-LINEAR LEAST SQUARES METHOD TO NON-ISOTHERMAL KINETICS

The general rate equation of the non-isothermal kinetics, in the framework of the reaction order model, has the known form:

$$\beta \frac{\mathrm{d}\alpha}{\mathrm{d}T} = Z\,\mathrm{e}^{-(E/RT)}(1-\alpha)^n \tag{18}$$

where β = the heating rate, α = the conversion degree, Z = the preexponential factor, E = the activation energy, n = the reaction order, T = absolute temperature and $R = 1.986$ calK^{-1} mol^{-1}
By integrating eqn (18), we get:

$$\mathrm{F}(\alpha) - \phi\left(-\frac{E}{RT}\right) = 0 \tag{19}$$

where

$$\mathrm{F}(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n}$$

The general form of eqn (19) is valid both for linear and for non-linear heating programmes.

The function ψ, as defined in the former section, has the particular form:

$$\psi = \mathrm{F}(\alpha) - \phi\left(-\frac{E}{RT}\right) = \mathrm{f}(\underbrace{\alpha, T,}_{x}\ \underbrace{n, E, Z}_{P}) = 0$$

Taking into account the experimental errors in determining the α_i, T_i values, as well as the approximate values of n, E and Z, it follows that $\psi \neq 0$. Using the non-linear least squares method, one can minimize the deviations from zero values of this function.

The particular form of system (13) is:

$$\begin{bmatrix} \mathrm{D1.D1} & \mathrm{D1.D2} & \mathrm{D1.D3} \\ \mathrm{D2.D1} & \mathrm{D2.D2} & \mathrm{D2.D3} \\ \mathrm{D3.D1} & \mathrm{D3.D2} & \mathrm{D3.D3} \end{bmatrix} \times \begin{bmatrix} \Delta n \\ \Delta Z \\ \Delta E \end{bmatrix} = - \begin{bmatrix} \mathrm{C1} \\ \mathrm{C2} \\ \mathrm{C3} \end{bmatrix} \tag{20}$$

where the notations (12) are still valid with $p_1 = n, p_2 = Z, p_3 = E$, and

$$\mathrm{CK} = \sum_{i=1}^{N} \mathrm{f}_i \frac{\partial \mathrm{f}_i}{\partial p_k}$$

For a linear heating programme:

$$\phi\left(-\frac{E}{RT}\right) = \frac{Z}{\beta} \int_0^T \mathrm{e}^{-(E/RT)}\, \mathrm{d}T \tag{21}$$

$$\left.\begin{aligned}
&\frac{\partial \mathrm{f}}{\partial E} = -\frac{\partial \phi}{\partial E} = -\frac{Z}{\beta} \int_0^T \frac{\partial}{\partial E}\left(\mathrm{e}^{-(E/RT)}\right) \mathrm{d}T = \frac{Z}{\beta}\frac{1}{RT} \int_0^T \mathrm{e}^{-(E/RT)}\, \mathrm{d}T \\
&\frac{\partial \mathrm{f}}{\partial Z} = -\frac{\partial \phi}{\partial Z} = -\frac{1}{\beta} \int_0^T \mathrm{e}^{-(E/RT)}\, \mathrm{d}T \\
&\frac{\partial \mathrm{f}}{\partial n} = \frac{\partial \mathrm{F}}{\partial n} = \begin{cases} n \neq 1 & \dfrac{1 - (1-\alpha)^{1-n} - [(1-\alpha)^{1-n} \ln(1-\alpha)]\,(1-n)}{(1-n)^2} \\[2ex] n = 1 & \dfrac{\ln^2(1-\alpha)}{2} \end{cases}
\end{aligned}\right\} \tag{22}$$

As regards a hyperbolic heating programme, for which $\beta = bT^2$,

$$\phi\left(-\frac{E}{RT}\right) = \frac{ZR}{\mathrm{b}E}\mathrm{e}^{-(E/RT)} \tag{23}$$

$$\left.\begin{aligned}
&\frac{\partial f}{\partial E} = -\frac{\partial \phi}{\partial E} = \frac{Z}{b}\frac{R}{E}\left(\frac{1}{E} + \frac{1}{RT}\right) e^{-(E/RT)} \\
&\frac{\partial f}{\partial Z} = -\frac{\partial \phi}{\partial Z} = -\frac{R}{bE} e^{-(E/RT)} \\
&\frac{\partial f}{\partial n} = \frac{\partial F}{\partial n} = \begin{cases} n \neq 1 & \dfrac{1-(1-\alpha)^{1-n} - [(1-\alpha)^{1-n}\ln(1-\alpha)](1-n)}{(1-n)^2} \\ n = 1 & \dfrac{\ln^2(1-\alpha)}{2} \end{cases}
\end{aligned}\right\} \quad (24)$$

4. FORTRAN PROGRAMME TO CALCULATE THE VALUES OF THE KINETIC PARAMETERS

On the basis of system (20), as well as of relationships (23) and (24), we worked out a programme whose logical diagram is given in Fig. 1.

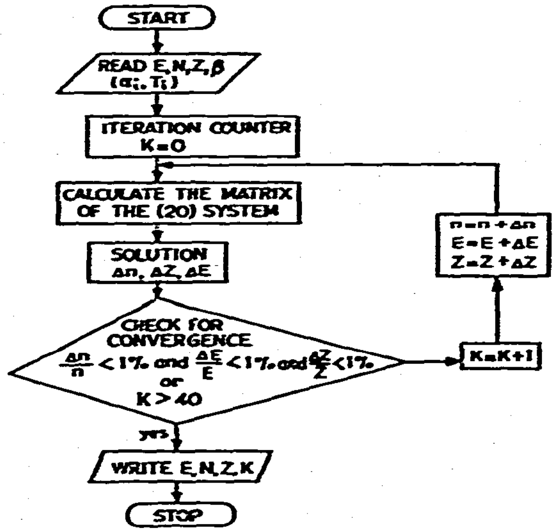

Fig. 1. Logical diagram.

5. EXAMPLE

The variant of the non-linear least squares method was applied to the non-isothermal kinetics of calcium oxalate monohydrate dehydration. The starting values of the kinetic parameters were obtained by using a hyperbolic heating programme[4] (Table 1).

The smooth convergency of the pre-exponential factor values are due to the very small values of the derivative

TABLE 1

THE STARTING VALUES, THE CORRECTIONS FOR FIVE ITERATIONS AND THE FINAL VALUES OF THE KINETIC PARAMETERS FOR THE CALCIUM OXALATE MONOHYDRATE DEHYDRATION

Initial values: $E_0 = 18{,}86$ kcal mole^{-1}; $n_0 = 1$; $Z_0 = 6{,}35 \cdot 10^6$ sec^{-1}.

Iteration No.	ΔE *(kcal mol^{-1})*	Δn	ΔZ *(10^6 sec^{-1})*
1	-0.964	-0.223	-6.994
2	$+0.038$	-0.0125	$+2.720$
3	-0.143	-0.0258	-0.222
4	$+0.014$	$+0.0016$	$+0.039$
5	-0.006	$+0.0024$	-0.013

Final values: $E = 17.80$ kcal mol^{-1}; $n = 0.74$; $Z = 1.88 \cdot 10^6$ sec^{-1}.

$$\frac{\partial f}{\partial Z}\left(\frac{\partial f}{\partial Z} \simeq 10^{-7}\right).$$

Thus the f function is quite insensitive to the changes of the pre-exponential factor values.

6. CONCLUSIONS

A variant of the non-linear least squares method to evaluate the kinetic parameters of the heterogeneous reactions under non-isothermal conditions, was worked out. The method was checked for the dehydration of calcium oxalate monohydrate.

REFERENCES

1 J. H. Flynn and L. A. Wall, *J. Res. Nat. Bur. Stand.*, 70A (1966) 487.
2 A. C. Norris, M. I. Pope, M. Selwood and M. D. Judd, *Thermal Analysis 4th ICTA*, Vol. 1, Academiai Kiado, Budapest, 1975, p. 65.
3 M. D. Judd and A. C. Norris, *J. Therm. Anal.*, 5 (1973) 179.
4 V. Marcu and E. Segal, *Revista Chim.*, in press.