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PSEUDO-INVERSE MATRIX METHOD – A DIRECT METHOD FOR NON-ISOTHERMAL KINETIC ANALYSIS

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Abstract

A new method is reported for the evaluation of non-isothermal kinetic data for various forms of the conversion function. The algorithm is based on a pseudo-inverse matrix method. A description of the algorithm and some calculation examples are presented.

Keywords: conversion function, non-isothermal kinetics

Introduction

When the integral form of the kinetic equation is used, the evaluation of non-isothermal kinetic parameters is based on various approximations of the temperature integral.

A conversion function based on the reaction order model is usually used. In order to discriminate between possible mechanisms, a non-linear regression procedure is frequently applied. However, this can lead to poorly-determined systems. Another difficulty is that the results are influenced to a certain extent by the initial estimate of the solution.

The method we propose is to solve an over-determined system of equations:

$$(\mathrm{d}\alpha/\mathrm{d}t)_i = k_i(T)f_i(\alpha) \qquad (1)$$

where i equations are to be considered. By solving this system, one can obtain the parameters from the Arrhenius expression $k(T)$, and also the parameters involved in the conversion function $f(\alpha)$.

This method furnishes approximate solutions of the system of equations.

The method

The method is based on a pseudo-inverse matrix method, i.e. on the solution of an over-determined system of equations.

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Given an m n matrix A, where $m>n$, and an m l vector b, we can find a vector x such that Ax is the best estimate of b.

For an over-determined system of equations, one cannot generally find an exact solution. However, we can find an approximate solution, the vector x, which can be evaluated in a least-squares approach such that the residual vector $r=Ax-b$ should be minimum [1]. In this case, the solution is equivalent to $(A^TA)x=A^Tb$, where A^T is the transposed of matrix A; this system can be solved in a classical way. In order to avoid a possible poorly-conditioned system, a relatively large number of equations are required ($m>10$ for $n=3$ to 4).

Equation (1) can be written as

$$\ln(\mathrm{d}\alpha/\mathrm{d}T)_i = \ln(A/a) - E/RT_i + \ln[f(\alpha)_i] \qquad (2)$$

where a is the heating rate (K s^{-1}), and the other notations have the usual meanings in chemical kinetics. The function $f(\alpha)$ may be more complex than the reaction order model one. For instance, for a conversion function of the type $f(\alpha) = \alpha^m(1-\alpha)^n$, relationship (2) becomes

$$\ln(\mathrm{d}\alpha/\mathrm{d}T)_i = \ln(A/a) - E/RT_i + m\ln(\alpha)_i + n\ln(1-\alpha)_i \qquad (3)$$

Thus, we can solve the system of equations (3) for i data points, except for $\alpha=0$ and $\alpha=1$. This system gives an approximate solution by solving $(A^TA\ )x=A^Tb$, where b has i components, each equal to $\ln(\mathrm{d}\alpha/\mathrm{d}T)_i$. The rectangular matrix A has i lines and the following elements for each line: 1, $-1/RT_i$, $\ln(\alpha_i)$ and $\ln(1-\alpha_i)$. The solution vector x contains the elements $\ln(A/a)$, E, m and n.

Results and discussion

On the basis of this method, we have developed a computer program which allows the evaluation of non-isothermal kinetic parameters and a discrimination between various mechanisms (this program, which has other capabilities, will be described elsewhere [2]). The conversion function used in our program is of the general form

$$f(\alpha) = a^m(1-\alpha)^n[-\ln(1-\alpha)]^p \qquad (4)$$

but (for numerical reasons) only a few parameters (n, m and/or p) are used in the calculations. We can therefore search for conversion functions such as α^m, $(1-\alpha)^n$, $[-\ln(1-\alpha)]^p$, $\alpha^m(1-\alpha)^n$, $\alpha^m[-\ln(1-\alpha)]^p$, and $(1-\alpha)^n[-\ln(1-\alpha)]^p$.

We present below results obtained with this method for several systems, in comparison with the methods of Coats-Redfern [3], Flynn-Wall [4], Achar [5] and Urbanovici-Segal [6]. For the reaction-order model, the data (100 pairs of data points) were simulated as temperature *vs.* conversion, with the following parameters $n=1.0$, $A=10^{12}$s^{-1} and $E=120$ kJ mol^{-1} for a heating rate of 5 K min^{-1}.

The parameters calculated for the simulated data are listed in Table 1.

Table 1 Values of non-isothermal kinetic parameters calculated by four methods (the data were simulated with the parameters n=1.0, A=10^{12} $s^{-1}$and E=120 kJ mol^{-1} for a heating rate of 5 K min^{-1})

	CR	*FW*	*A*	*US*
E/kJ mol^{-1}	119.8±0.2	120.4±0.1	120.0±0.03	116.5±0.05
$10^{-12}A/s^{-1}$	0.89±0.10	1.12±0.04	1.02±0.03	0.35±0.04
n	1.0	1.0	1.0	0.9
r	0.999999	0.999998	0.999999	0.99992

As may be expected, the data are described well by these methods (for the reaction order conversion function).

With the pseudo-inverse matrix method and various conversion functions, we obtained the parameters listed in Table 2. The mean deviation is the mean difference between the experimental and computed free term b. This is an indication (but not a criterion) of the quality of the data obtained. For other combinations of conversion functions containing the term $[-\ln(1-\alpha)]^p$, the calculations are not possible (the exponentional factor exceeds $10^{100}s^{-1}$). This table reveals a good correlation between the calculated and simulated parameters, and also the fact that the conversion function is that of the reaction order model.

Table 2 Values of non-isothermal kinetic parameters calculated with the pseudo-inverse matrix method (the data were simulated with the parameters n=1.0, A=10^{12} $s^{-1}$and E=120 kJ mol^{-1} for a heating rate of 5 K min^{-1})

	$(1-\alpha)^n$	$(1-\alpha)^n\alpha^m$
E/kJ mol^{-1}	118.8	132.6
$10^{-12}A/s^{-1}$	0.72	30.8
n, m	0.98	1.02, -0.1
Mean dev. (%)	1.75	2.7

Table 3 Values of non-isothermal kinetic parameters of decomposition of calcium oxalate, calculated with the pseudo-inverse matrix method

	$(1-\alpha)^n$	$\alpha^m[-\ln(1-\alpha)]^p$
E/kJ mol^{-1}	87.6	360.1
A/s^{-1}	$5.3\cdot10^6$	$3.09\cdot10^{38}$
n, m, p	0.72, –, –	–, 2., –4.6
Mean dev. (%)	3.0	2.5

With the pseudo-inverse matrix method, we obtained the parameters listed in Table 3 for the decomposition of calcium oxalate. For other combinations of the conversion functions, the calculations lead to inacceptable results. It may be seen in Table 3 that the conversion function is either of the reaction order type or of the $\alpha^m[-\ln(1-\alpha)]^p$ type. For the conversion function of $\alpha^m[-\ln(1-\alpha)]^p$ type, we consider that the paramters obtained are somewhat unusual (the activation energy >80 Kcal mol^{-1}, the value for p, etc.). Accordingly, we take into account only the values for the reaction order model, even if the mean deviation is slightly lower for the other function. As already stated, the mean deviation is an indication, but not a criterion. This Table demonstrates that the parameters obtained for the conversion function $(1-\alpha)^n$ are more probably the true ones.

Table 4 Values of non-isothermal kinetic parameters for the decomposition of calcium oxalate

	CR	*FW*	*A*	*US*
E/kJ mol^{-1}	98.2±0.6	98.8±0.1	96.5±0.2	96.9±0.2
$10^{-7}A$/s^{-1}	6.9±4.0	9.8±0.5	5.3±3.0	5.0±0.9
n	0.9	0.8	0.9	0.8
r	0.999843	0.999867	0.999591	0.999591

For the same reaction, the classical methods gave the results presented in Table 4. There is a slight difference between the parameters computed with the pseudo-inverse matrix and those obtained by linearization. This difference (not a significant one) can be accounted for by a compensation effect. Figure 1 presents the (α, T) curves resulting from the Coats-Redfern and pseudo-inverse methods in comparison with the experimental points. The results obtained with the

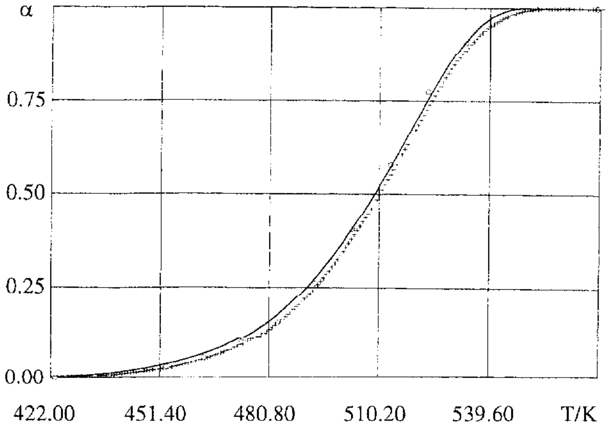

Fig. 1 (α, T) curves for the dehydration of calcium oxalate, obtained with the Coats-Redfern method (crosses) and the pseudo-inverse method (continuous line) in comparison with the experimental points (circles)

pseudo-inverse matrix method may be seen to describe the experimental data satisfactorily. This confirms that the conversion function and the parameters obtained are correct.

Conclusions

A method for the evaluation of non-isothermal kinetic parameters and to discriminate between mechanisms is presented. The algorithm, checked with simulated data, gives good results in comparison with other methods.

The advantage of this method is that the results are not influenced by the initial estimation as is the case with non-linear regression methods.

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