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APPLICATION OF THE PSEUDO-INVERSE MATRIX METHOD IN NON-ISOTHERMAL KINETIC ANALYSIS

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Abstract

A method is proposed for evaluation of the activation parameters for reactions which occur under non-isothermal conditions. This method can discriminate between possible differential conversion functions. The proposed method, which was coded into a software package available to the scientific community, is designed to solve an overdetermined systems of equations:

$$\mathrm{d}a_i/\mathrm{d}t=k(T_i)f(a_i)$$

where *i* equations are to be considered (*i* can be the number of experimental points). Solution of this overdetermined system with a pseudo-inverse matrix method furnishes the activation parameters and the parameters of the conversion function $f(a)$. Some examples of application of this method in non-isothermal kinetic analysis are presented.

Keywords: kinetic parameters, non-isothermal analysis

Introduction

The evaluation of non-isothermal kinetic parameters is based on various approximations of the temperature integral; the most common conversion function used is that of the reaction order model. This choice of the reaction model can lead to errors in the interpretation of the experimental data as the mechanism of the reaction can differ from that of the reaction order model. The first step in the evaluation of the activation parameters of a solid-state reaction, therefore, should be the establishment of the reaction mechanism. In order to discriminate between possible mechanisms, a non-linear regression procedure can be applied. However, the results are influenced by the initial estimate of the solution. The method proposed here, which is basically one of non-linear least squares, is to solve an overdetermined system of equations:

$$\left(\frac{\mathrm{d}a}{\mathrm{d}t}\right)_i = k_i(T)f_i(a) \qquad (1)$$

where *i* equations are to be considered.

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The differential form is used and no approximation are made in the evaluations of the activation parameters. One way to evaluate the activation parameters is to use a linear form of Eq. (1), where possible. The choice of different forms of the conversion function, the evaluation of the activation parameters and an estimate of the precision can lead to a discrimination between the possible reaction mechanisms. Similarly, an overdetermined system such as Eq. (1) can be solved for various conversion functions and the activation parameters can be obtained for each of the conversion functions used. The problem lies in the selection of the best solution. Our approach was mainly concerned with the elaboration of the algorithm, but less with the validity of the criteria we propose. The standard deviation should be a statistical criterion, but the values obtained in a non-linear regression sometimes have no physical-chemical meaning, although the fit is better in a statistical sense [2]. This may arise from the limitations in modelling the physical process.

The method is based on the pseudo-inverse matrix method, i.e. on the solution of an overdetermined system of equations. Given an $m\times n$ matrix $\mathbf{A}$, where $m>n$, and an $m\times l$ vector $\mathbf{b}$, we can find a vector $\mathbf{x}$ such that $\mathbf{A}\times\mathbf{x}$ is the best estimate of $\mathbf{b}$. We can find an approximate solution, the vector $\mathbf{x}$, which can be evaluated in a least-squares approach such that the residual vector $r=\mathbf{A}\times\mathbf{x}-\mathbf{b}$ should be minimum [1].

The system (1) can be written as:

$$\ln\left(\frac{\mathrm{d}a}{\mathrm{d}T}\right)_{\mathrm{i}} = \ln\frac{A}{a} - \frac{E}{RT_{\mathrm{i}}} + \ln f(a)_{\mathrm{i}} \tag{2}$$

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

$$\ln\left(\frac{\mathrm{d}t}{\mathrm{d}T}\right)_{\mathrm{i}} = \ln\frac{A}{a} - \frac{E}{RT_{\mathrm{i}}} + m\ln a_{\mathrm{i}} + n\ln(1-a)_{\mathrm{i}} \tag{3}$$

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

Results and discussion

On the basis of this method, we have worked out a computer program which allows an evaluation of the non-isothermal kinetic parameters, and a discrimination between various mechanisms [2]. The conversion function used in this program is of the general form

$$f(a) = a^{\mathrm{m}}(1-a)^{\mathrm{n}}[-\ln(1-a)]^{\mathrm{p}} \tag{4}$$

able 1 Values of non-isothermal kinetic parameters calculated by means of the Coats-Redfern method for the four simulated data sets (the data were simulated with the following parameters: n=0. 0.66. 1.0 and 2.0. $A=10^{12}$ s^{-1} and E=120.0 kJ mol^{-1} for a heating rate of 5 K min^{-1})

Parameter	1	2	3	4
E/kJ mol^{-1}	119.8±0.1	119.7±0.1	118.8±0.03	119.8±0.05
$A\cdot 10^{-12}$/s^{-1}	0.9±0.03	0.88±0.03	0.89±0.03	0.91±0.02
n	0.00	0.66	1.00	2.00
r	0.9999998	0.9999977	0.9999995	0.9999792

able 2 Values of non-isothermal kinetic parameters calculated by means of the pseudo-inverse matrix method (1, 2, 3 and 4 denote the data sets used in the calculations; the data were simulated with the following parameters: n=0, 0.66, 1.0 and 2.0, $A=10^{-12}$ s^{-1} and E=120.0 kJ mol^{-1} for a heating rate of 5 K min^{-1}). For the more complex conversion functions involving two parameters, all the results were meaningless (negative activation energy, overflow in the computing)

Parameter	1	2	3	4
		Conversion a^m		
E/kJ mol^{-1}	101.7	–350.6	–286.1	–139.0
A/s^{-1}	$6.80\cdot 10^{9}$	$2.88\cdot 10^{-44}$	$1.20\cdot 10^{-36}$	$2.3\cdot 10^{-20}$
m	0.14	3.76	3.25	2.10
dev.	17.4	>100	>100	>100
		Conversion $(1-a)^n$		
E/kJ mol^{-1}	120.32	119.77	119.60	125.8
A/s^{-1}	$1.14\cdot 10^{12}$	$0.94\cdot 10^{12}$	$0.902\cdot 10^{12}$	$6.53\cdot 10^{12}$
n	0.066	0.638	0.992	2.084
dev.	3	2.8	2.6	>100
		Conversion $[-\ln(1-a)]^p$		
E/kJ mol^{-1}	138.7	653.3	overflow	–251.4
A/s^{-1}	$1.70\cdot 10^{14}$	$1.18\cdot 10^{75}$	–	$1.11\cdot 10^{34}$
p	–0.14	–4.23	–	2.95
dev.	2.5	7.1	–	>100

In the actual version of the program, we can search for conversion functions with two arameters such as

$$a^m,\ (1-a)^n,\ [-\ln(1-a)]^p,\ a^m(1-a)^n,\ a^m[-\ln(1-a)]^p,\ (1-a)^n[-\ln(1-a)]^p.$$

In the following, the results obtained with the use of this method for several systems are presented, in comparison with the Coats-Redfern [3] method. Four data sets were simulated with the following parameters: heating rate 5 K min^{-1}, n=0, 0.66, 1 and 2, $A=10^{12}$ s^{-1} and E=120 kJ mol^{-1}. The data were simulated as conversion, temperature data and subsequently used for Coats-Redfern evaluation. Between 130 and 200 data points were simulated at 1 K steps on the condition that the degree of conversion differed by more than 10^{-5} from the adjacent value. Points closer than 10^{-5} in conversion were skipped. The parameters calculated with the Coats-Redfern model are listed in Table 1. As can be expected, the data are well described by this method (for the reaction order conversion function). The agreement between the simulated and computed data is very good (in the simulation, 5 terms in the asymptotic approximation were considered).

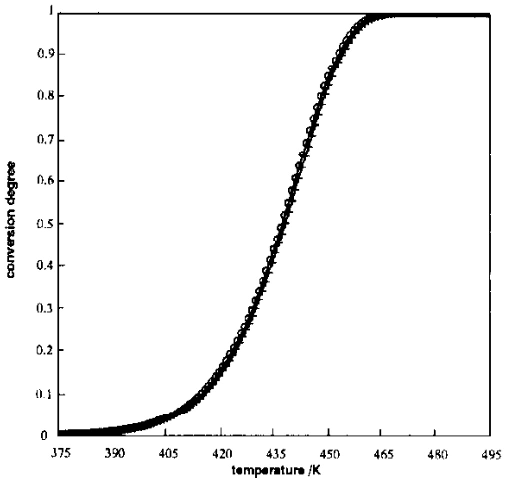

Fig. 1 (α, T) curves for the simulated data (line) n=1, A, E; data obtained from the Coats-Redfern method (crosses) and the pseudo-inverse method (circles)

With the pseudo-inverse matrix method, various conversion functions were used to obtain the parameters listed in Table 2. The differential values needed in the algorithm were obtained numerical differentiation. This can induce errors in the parameters obtained. However, under working conditions the experimental data are obtained directly as differential values from the DTG signal. Mean deviation stands here for 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. 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. Some limitations arise from the chosen data sets: with increase in the reaction order, the (conversion, temperature) dependence is smoother and the conversion does not change much with temperature at the beginning and the end of the reaction. This gives very close points in dα/dT (we set an arbitrary limit at a 10^{-5} difference in conversion and at least a 1 K difference in temperature). Another drawback is the value of the coefficient matrix in the case of the conversion function $[-\ln(1-\alpha)]^p$, when an ill-determined system can often arise.

However, it may be seen that the results obtained with the pseudo-inverse matrix method satisfactorily describe the experimental data (the experimental and simu-ated values of the conversion function *vs.* temperature are shown in Fig. 1). This method also checks that the conversion function and the parameters obtained are correct.

Conclusions

A method for evaluation of the non-isothermal kinetic parameters and a procedure to discriminate between mechanisms are presented.

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