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Note

CRITICAL REMARKS ON THE SIMULTANEOUS EVALUATION OF NON-ISOTHERMAL KINETIC PARAMETERS AS SOLUTIONS FOR SYSTEMS OF LINEAR EQUATIONS

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Since the appearance of non-isothermal methods to evaluate kinetic parameters, a lot of work has been performed with their intensive use [1,2]. The "exponential" development of non-isothermal kinetic analysis is mainly due to its advantages, e.g., the rapid analysis of a whole temperature interval where a chemical reaction or a physical process takes place. After a certain accumulation of kinetic data, as is usual in science, the appearance of some critical analyses concerning the methodology applied in non-isothermal kinetics are noticed. Among the more recent and comprehensive analyses worthy of mention are those by Šesták [3] and Arnold et al. [4].

This paper deals with the possibility of evaluating a number of non-isothermal kinetic parameters in connection with the errors inherent in the experimental measurements. As will be shown, such a problem is particularly significant for heterogeneous processes whose kinetics are not described by the reaction order model (characterized only by three kinetic parameters), but by more complicated equations with a higher number of kinetic parameters.

As in many non-isothermal kinetic investigations, we shall start from the rate equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} \mathrm{f}(\alpha) \mathrm{e}^{-E/RT} \tag{1}$$

where the symbols have their usual meanings, and for simplicity, one considers [5,6]

$$A = A_r T^r \tag{2}$$

and

$$\mathrm{f}(\alpha) = (1-\alpha)^n \alpha^m \left[\ln \frac{1}{1-\alpha}\right]^q \tag{3}$$

Equation (1) can be brought into a linear form. Indeed, introducing eqns. (2)

and (3) in (1), and taking logarithms gives

$$\log\frac{A_r}{\beta} + r\log T - \frac{E}{2.303} + n\log(l-\alpha) + m\log\alpha$$

$$+p\log\left[\ln\frac{1}{1-\alpha}\right] = \log\frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{4}$$

Thus, in principle, as α, T and $\mathrm{d}\alpha/\mathrm{d}T$ are experimentally measurable, eqn. (4) allows a system of linear equations to be written whose solutions are the values of the kinetic parameters n, A, E, r, m and p. As will be shown in the following, the number of solutions cannot be arbitrarily high, but is limited by the experimental errors.

In order to illustrate this, some basic mathematics have to be considered [7,8].

(1) A system of n linear equations with n unknowns

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \ldots + a_{1n}x_n &= b_1 \\ a_{21}x_1 + a_{22}x_2 + \ldots + a_{2n}x_n &= b_2 \\ a_{n1}x_1 + a_{n2}x_2 + \ldots + a_{nn}x_n &= b_n \end{aligned} \tag{5}$$

can be written in matrix form as [7]

$$\mathbf{A}\vec{X} = \vec{b} \tag{6}$$

where **A** is the coefficients matrix

$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} & \cdots & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & \cdots & a_{nn} \end{bmatrix} \tag{7}$$

$\vec{b}$ is the vector of the free terms

$$\vec{b} = \begin{bmatrix} b_1 \\ b_n \\ \vdots \\ b_n \end{bmatrix} \tag{8}$$

and $\vec{X}$ is the vector of the unknowns

$$\vec{X} = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix} \tag{9}$$

(2) The inverse of matrix **A**, $\mathbf{A}^{-1}$, is given by [7]

$$\mathbf{A}\mathbf{A}^{-1} = \mathbf{A}^{-1}\mathbf{A} = \mathbf{E} \tag{10}$$

the identity matrix **E** being given by

$$\mathbf{E}=\begin{bmatrix}1 & 0 & \dots & \dots & 0\\ 0 & 1 & \dots & \dots & 0\\ 0 & 0 & \dots & \dots & 1\end{bmatrix} \tag{11}$$

According to matrix algebra [7]

$$\mathbf{A}^{-1}=\begin{bmatrix}\frac{A_{11}}{\Delta} & \frac{A_{21}}{\Delta} & \dots & \dots & \frac{A_{n1}}{\Delta}\\ \frac{A_{12}}{\Delta} & \frac{A_{22}}{\Delta} & \dots & \dots & \frac{A_{n2}}{\Delta}\\ \frac{A_{1n}}{\Delta} & \frac{A_{2n}}{\Delta} & \dots & \dots & \frac{A_{nn}}{\Delta}\end{bmatrix} \tag{12}$$

where

$$\Delta=\det\mathbf{A}\neq 0 \tag{13}$$

and A_{ij} are the cofactors of the matrix elements a_{ij}.

(3) The length, X, of a vector $\vec{X}(x_1, x_2, \dots, x_n)$ is given by [9]

$$X=(\vec{X},\vec{X})^{1/2} \tag{14}$$

where the parentheses and the comma indicate the scalar product, thus

$$X=\left(\sum_{i=1}^{n} x_i^2\right)^{1/2} \tag{15}$$

To appreciate the error of the solution $\vec{X}$ of the system (6) one has to use the conditioning rules [9]. If, for instance, in the system of linear equations (6) small changes of the elements in matrix **A** or of the vector $\vec{b}$ induce important changes in the solutions, the system is called "bad conditioned". In the opposite case, the system is considered as "good conditioned".

To introduce a quantitative conditioning criterion one has to consider in eqn. (6) small increments Δa_{ij} for the elements of matrix **A** and Δb_i, for the elements of the vector $\vec{b}$, i.e.

$$(\mathbf{A}+\Delta A)(\vec{X}+\Delta\vec{X})=\vec{b}+\Delta\vec{b} \tag{16}$$

Taking into account eqn. (6) one gets

$$\mathbf{A}\,\Delta\vec{X}+\Delta A\Delta\vec{X}=\Delta\vec{b}-\Delta A\vec{X} \tag{17}$$

If the matrices **A** and $\mathbf{A}+\Delta A$ are square and non-singular (i.e., $\det\mathbf{A}\neq 0$ and $\det(\mathbf{A}+\Delta A)\neq 0$), through the multiplication of relationship (17) by $(\mathbf{A}+\Delta A)^{-1}$, we get

$$\Delta\vec{X}=(\mathbf{A}+\Delta A)^{-1}(\Delta\vec{b}-\Delta A\vec{X}) \tag{18}$$

or

$$\Delta\vec{X}=(\mathbf{E}+\mathbf{A}^{-1}\Delta A)^{-1}\mathbf{A}^{-1}(\Delta\vec{b}-\Delta A\vec{X}) \tag{19}$$

Relationship (19) for small enough ΔA values, becomes

$$\Delta \vec{X} \simeq \mathbf{A}^{-1} (\Delta \vec{b} - \Delta A \vec{X}) \tag{20}$$

According to this last result, if det **A** has a small value, and thus det $\mathbf{A}^{-1}$ has a high value, matrix **A** contains elements with high values.

In order to introduce a conditioning criterion we shall use the normalized determinant of the matrix **A**, det $\mathbf{A}_{\mathrm{N}}$, where $\mathbf{A}_{\mathrm{N}}$ represents the normalized matrix. This matrix can be obtained using the relationship

$$\det \mathbf{A}_{\mathrm{N}} = \alpha_A^n \det \mathbf{A} \tag{21}$$

where

$$\alpha_A^n = \left[\prod_{j=1}^{n} \left(\vec{A}_j, \vec{A}_j \right) \right]^{-1/2} = \left[\prod_{j=1}^{n} \left(\sum_{i=1}^{n} a_{ij}^2 \right) \right]^{-1/2} \tag{22}$$

In terms of det $\mathbf{A}_{\mathrm{N}}$, the conditioning criterion is: $|\det \mathbf{A}_{\mathrm{N}}| = 1$ for good conditioned systems of linear equations; $|\det \mathbf{A}_{\mathrm{N}}| = 0$ for bad conditioned systems of linear equations. In fact the figures 0 and 1 are limits between which the conditioning of the searched system can be realized.

The above-mentioned conditioning criterion was applied for the system of linear equations used to evaluate the kinetic parameters of the dehydration of calcium oxalate monohydrate.

Equation (4), with $r = m = p = 0$, allows the evaluation of only three kinetic parameters A, n and E (in fact log A/β, n and $E/2.303R$). In order to do this, the following experimental data were used.

T(K)	493	503	513
α	0.278	0.415	0.585

For this case

$$\mathbf{A} = \begin{bmatrix} 1 & \log 0.722 & \frac{1}{493} \\ 1 & \log 0.585 & \frac{1}{503} \\ 1 & \log 0.415 & \frac{1}{513} \end{bmatrix}$$

and $|\det \mathbf{A}_{\mathrm{N}}| = 0.476$.

Thus, the system of three equations with three unknowns can be solved; the values of the kinetic parameters being affected to some extent by the inherent errors. If, in eqn. (4), $m = p = 0$, i.e., four kinetic parameters have to be evaluated (A_r, n, E, r) one more pair of (α, T) values must be used, as in the following table of experimental data.

T(K)	483	493	505	513
α	0.166	0.278	0.415	0.585

The matrix **A** for the system of four linear equations with four unknowns, takes, in this case, the form

$$A = \begin{bmatrix} 1 & \log 0.834 & \log 483 & \frac{1}{483} \\ 1 & \log 0.722 & \log 493 & \frac{1}{493} \\ 1 & \log 0.585 & \log 503 & \frac{1}{503} \\ 1 & \log 0.415 & \log 513 & \frac{1}{513} \end{bmatrix}$$

and $|\det A_N| = 0.102$. Thus, the addition of one more parameter determined a bad conditioning of the system.

These considerations were confirmed by calculations which did not allow the evaluation of more than three kinetic parameters.

This explains perhaps (but does not justify) the use of a conversion function corresponding to the reaction-order model for heterogeneous solid-state reactions instead of other conversion functions which adequately describe such processes.

The criticism presented should not be considered as a destructive one, since non-isothermal kinetics have a past, a present, and a future. It is the task of research workers to be aware of this, as well as the other critical standpoints, and to seek adequate solutions of the problems raised by them.

CONCLUSIONS

An analysis concerning the simultaneous evaluation of a set of kinetic parameters was performed.

A criterion, limiting the number of kinetic parameters which can be accurately evaluated was discussed.

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