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IMPROVED PARAMETER ESTIMATION IN ARRHENIUS TYPE MODELS

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INTRODUCTION

In order to express temperature dependence of the rate constant K in a number of kinetic processes /see /1// frequently the familiar Arrhenius equation is being used

$$K = K_o \cdot \exp /-E/RT/ \qquad 1$$

where K_o is a preexponential factor /which is connected with entropy of the kinetic process according to absolute reaction rates theory/, R is the gas constant and T is the absolute temperature.

Equation 1 is implemented in a broad area of thermal analysis /1/. In estimating the parameters K_o and E normally from the set of n experimental points $/K_i, T_i/_{i=1,\dots,N}$ is started and a number of statistical techniques commonly based on the least squares principle are utilized.

In the present work basic methods for parameter estimation in equation 1 are analyzed, considering various assumptions on measurement errors of the rate constants K_i with respect to their physical nature. An algorithm is suggested enabling to find convenient model of measurement errors with simultaneous estimation to the parameters K_o, E.

ESTIMATION PROCEDURES

The classical method of estimating the parameters in equation 1 is represented by the least squares technique /LST/ which is based on minimization of the criterion

$$S/\underline{a}/ = \sum_{i=1}^{n} [K_i - K/T_i/]^2 \qquad 2$$

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where $K/T_i/ = K_o . \exp /-E/RT_i/$ are the theoretical values. Minimization of equation 2 necessitates application of nonlinear optimization methods which are tedious and time consuming. Moreover, due to strong multicolinearity /i. e. strong dependence between the parameters K_o and E/ the minimization of equation 2 is complicated and frequently leads to finding a false optimum.

In order to simplify the calculations linearization of equation 1 having the form

$$\ln K = \ln K_o - E/RT \qquad 3$$

is used. Instead of iterative minimization of equation 2 the following relationship is minimized

$$S_L /\underline{a}/ = \sum_{i=1}^{n} \left[\ln K_i - \ln K_o + E/RT_i\right]^2 \qquad 4$$

Equation 4 is a well-known criterion of linear least squares /minimization according to $\ln K_o$ and E leads to a set of two linear equations/. The estimates $\widehat{\ln K_o}$ and $\hat{E}$ may then be determined by substituting into the well-known relations for estimation of slope and intercept of the straight line by the least squares.

A survey of further techniques which eliminate partly the linearizing bias is given in the work /2/. To compare the properties of these estimates statistical properties of random quantities K_i should be analyzed.

CASE OF ADDITIVE ERRORS

In this case the following measurement model is assumed to hold

$$K_i = K_o . \exp /-E/RT_i/ + \varepsilon_i = K/T_i/ + \varepsilon_i \qquad 5$$

Random errors ε_i possess the following basic properties

i/ zero mean values $E/\varepsilon_i/ = \emptyset$ /the correct model/ 1.

ii/ constant variance $E/\varepsilon_i^2/ = \sigma^2 < \infty$ /the homoskedasticity model/

iii/ zero covariances $E/\varepsilon_i, \varepsilon_j/ = \emptyset$, $i \neq j = 1,\dots,m$ /independent errors/

Provided that errors ε_i are normally distributed the estimates with maximum likelihood $\hat{K}_o$, $\hat{E}$ may be obtained by maximizing the likelihood function

$$L/K_o,E/ = -\frac{n}{2}\ln /2\pi/ - \frac{n}{2}\ln \sigma^2 - \frac{1}{2\sigma^2} S/\hat{\underline{a}}/ \qquad 6$$

where $S/\hat{\underline{a}}/$ is the minimum value of equation 2. Following this assumption on errors ε_i leads to classical least squares with maximum likelihood estimates of K_o, E. The problem often met with in practice is that the error variance increases with raising true value $K/T_i/$ /relative precision is constant/. This case is solved in work /6/.

The additive measurement model 5 has certain restrictions. Due to additive nature of ε_i /random errors defined on the whole real line $\langle -\infty, \infty \rangle$/ the values K_i are not restricted as far as their sign is concerned. Considering physical nature of measured rate constants K_i they cannot be negative either. In this respect all techniques based on validity of equation 5 are not correct.

CASE OF MULTIPLICATIVE ERRORS

Here, it is supposed that the measurement model having the form

$$K_i = K/T_i/ \cdot \eta_i = K/T_i/ \cdot \exp /\varepsilon_i/ \qquad 7$$

is valid, where ε_i have the same properties as random errors in equation 5, i. e. they are independent having zero mean with constant variance. It may easily be derived that this model corresponds to the likelihood function, viz.

$$L_M/K_o,E/ = -\frac{n}{2}\ln /2\pi/ - \frac{n}{2}\ln \sigma^2 - \sum \ln K_i - \frac{1}{2\sigma^2} S_L /\hat{\underline{a}}/ \qquad 8$$

where $S_L /\hat{\underline{a}}/$ is defined by equation 4. It follows that the parameter estimates $\widehat{\ln K_o}$ and $\hat{E}$ with maximum likelihood are determined by simple substitution into the relations for slope and intercept estimates of straight line 3 by least squares. Among main advantages of the multiplicative model the following can be stated

- random quantities /measured rate constants/ K_i are always positive
- variances of K_i are not constant but they represent an increasing function of true values $K/T_i/$.

Moreover, provided that this measurement model is valid, linearization defined in equation 3 is correct and the parameter estimation problem becomes trivial.

IMPROVED PROCEDURE FOR PARAMETER ESTIMATION

From the above it follows that assumptions on measurement errors strongly affect quality of the estimates. For this reason the method has been chosen that enables to find suitable model type with simultaneous determination parameter estimates having maximum likelihood /see /4//.

It can be supposed that a power transformation

$$g_{\lambda}/K_i/ = g_{\lambda}\left[K/T_i/\right] + \varepsilon_i \qquad 9$$

exists, where ε_i have the same properties as in equation 5 and are additive. In a number of works /see /5// $g_{\lambda}/x/$ is selected, viz.

$$g_{\lambda}/x/ = \begin{cases} /x^{\lambda} - 1/ / \lambda & \text{for } \lambda \neq \emptyset \\ \ln x & \text{for } \lambda = \emptyset \end{cases} \qquad 10$$

It is obvious that for $\lambda = 1$ additive measurement model is defined by equation 9 /i. e. equation 5/ and for $\lambda = \emptyset$ the multiplicative one /equation 7/. For the rest of λ continuous family of functions dependent on single parameter λ are defined. The corresponding likelihood function L_K $/K_o,E,\lambda/$ may be expressed·

$$L_K /K_o,E,\lambda/ = -\frac{n}{2} \ln /2\pi\sigma^2/ + /\lambda - 1/ \sum_{i=1}^{n} \ln K_i - S_{\lambda}/\underline{a}/ \qquad 11$$

$$\text{where } S_{\lambda} /\underline{a}/ = \sum_{i=1}^{n} \left[g_{\lambda}/K_i/ - g_{\lambda}/K/T_i//\right]^2. \qquad 11a$$

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