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Optimum reference temperature for reparameterization of the Arrhenius equation. Part 2: Problems involving multiple reparameterizations

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ABSTRACT

Existence of high parameter correlations is one of the major problems during parameter estimation. This is particularly true when the mathematical model presents one or more kinetic constants that depend on temperature, as defined by the Arrhenius equation. In a recent work, Schwaab and Pinto [2007. Optimum reference temperature for reparameterization of the Arrhenius equation. Part 1: problems involving one kinetic constant. Chemical Engineering Science 62, 2750–2764] showed that an optimum reference temperature can be defined for reparameterization of the Arrhenius equation and elimination of parameter correlation, when the model contains a single kinetic constant. However, when the model contains more than one kinetic constant, the number of parameter correlations is larger than the number of reference temperatures that can be defined; consequently, it becomes impossible to eliminate all the parameter correlations simultaneously. For this reason, in this work different norms are defined for the parameter correlation matrix and are used to allow for minimization of the parameter correlations through manipulation of reference temperatures. Three parameter estimation problems are used to illustrate the use of the proposed two-step parameter estimation procedure and to show that the minimization of parameter correlations and relative errors are indeed possible through proper manipulation of reference temperatures in problems involving multiple model parameters.

1. Introduction

Attempting to explain and control the universe that surrounds us, researchers develop models in order to characterize and predict the evolution of physical phenomena. This way, scientific theories and analysis of process behavior rely heavily on the availability of sound mathematical models. Commonly, mathematical models contain variables that cannot be measured directly. The values of these variables, called model parameters, can be estimated from experimental data with the help of parameter estimation procedures, which consist in minimizing some sort of objective function that takes into account the difference between model responses and experimental observations. The objective function can be defined as the simple least squares function or, for more involving computations, as the maximum likelihood function (Bard, 1974).

A common model that is used to describe the temperature dependence of reaction rates in kinetic problems is the well-known Arrhenius equation:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{1}$$

where k is the rate constant (or the specific reaction rate), T is the absolute temperature, R is the ideal gas constant, k_0 is the frequency (or pre-exponential) factor and E is the activation energy. Both k_0 and E are the parameters of the Arrhenius equation, usually estimated from available experimental data.

Unfortunately, the intrinsic mathematical structure of this equation introduces a very strong dependence between the parameters k_0 and E. This dependence, called parameter correlation, makes the estimation of the correct values of the model parameters very hard. In order to overcome this difficulty, several works suggested the reparameterization of the Arrhenius equation by introducing a reference temperature in the form (Box, 1960; Himmelblau, 1970; Pritchard and Bacon, 1975):

$$k = k_{\text{ref}} \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right] \tag{2a}$$

$$k = \exp\left[A - \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right] \tag{2b}$$

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$$k = k_{\text{ref}} \exp\left[B\left(\frac{T - T_{\text{ref}}}{T}\right)\right] \tag{2c}$$

$$k = \exp\left[A + B\left(\frac{T - T_{\text{ref}}}{T}\right)\right] \tag{2d}$$

where the parameters of the reparameterized equations can be related to the parameters of the traditional Arrhenius equation as

$$k_{\text{ref}} = k_0 \exp\left(-\frac{E}{RT_{\text{ref}}}\right) \tag{3a}$$

$$A = \ln(k_{\text{ref}}) = \ln(k_0) - \frac{E}{RT_{\text{ref}}} \tag{3b}$$

$$B = \frac{E}{RT_{\text{ref}}} \tag{3c}$$

The introduction of the reference temperature into the Arrhenius equation allows for reduction of the parameter correlation and, consequently, for reduction of the computational effort required for estimation of model parameters (Espie and Macchietto, 1988) and improvement of the elliptic representation of the confidence regions of parameter estimates (Watts, 1994).

The reference temperature is usually defined as a suitable average temperature of the analyzed experimental data. For instance, Veglio et al. (2001) suggested the use of the inverse average:

$$\frac{1}{T_{\text{ref}}} = \frac{1}{\text{NE}} \sum_{i=1}^{\text{NE}} \frac{1}{T_i} \tag{4}$$

where NE is the number of experimental temperature values and T_i is the temperature for individual experiments.

In a previous work, Schwaab and Pinto (2007) showed that the proper definition of the reference temperature can eliminate the parameter correlation in kinetic models containing a single kinetic constant. It was shown both analytically and numerically that proper definition of reference temperature allows for elimination of the parameter correlation and simultaneous improvement of the precision of the parameter estimates.

When the number of kinetic constants (N) is larger than 1, the number of parameter correlations is equal to $N(2N-1)$, which may be much larger than N (that is, much larger than the number of reference temperatures). Therefore, the procedure proposed by Schwaab and Pinto (2007) cannot guarantee the simultaneous elimination of all parameter correlations in these cases. As a consequence, it becomes necessary to define a proper norm for the parameter correlation matrix in order to perform the minimization of parameter correlations appropriately.

In this work, the two-step parameter estimation procedure proposed by Schwaab and Pinto (2007) is extended in order to consider problems where multiple kinetic constant are present. Different norms are defined for the parameter correlation matrix and examined during minimization of the parameter correlation. Despite the fact that simultaneous elimination of all parameter correlations is not possible, it is shown here that the correlations can be significantly reduced when the numerical procedure is used to provide the proper definition of the reference temperatures.

2. Parameter estimation

The parameter estimation procedure consists in minimizing an objective function that takes into account the deviations between the experimental values and the model predictions through manipulation of model parameters. Assuming that independent variables **x** are free of errors, that experiments are performed independently and that dependent variables **y** are subject to experimental fluctuations that follow the normal distribution with known covariance matrix, then the maximum likelihood estimation consists in minimizing the following equation:

$$S(\boldsymbol{\theta}) = \sum_{i=1}^{\text{NE}} [\mathbf{y}_i^e - \mathbf{y}_i^m(\mathbf{x}_i, \boldsymbol{\theta})]^{\text{T}} \mathbf{V}_i^{-1} [\mathbf{y}_i^e - \mathbf{y}_i^m(\mathbf{x}_i, \boldsymbol{\theta})] \tag{5}$$

where $S(\boldsymbol{\theta})$ is the objective function to be minimized with respect to the parameter vector $\boldsymbol{\theta}$, $\mathbf{y}_i^e$ and $\mathbf{y}_i^m$ are the vectors of experimental observations and model responses at experimental condition i and NE is the total number of experiments. $\mathbf{V}_i$ is the covariance matrix of experimental observations at experimental condition i. Although it is possible to derive analytical solutions for linear models, the minimization of the objective function is usually performed with the help of appropriate numerical procedures, such as the traditional Newton methods, direct search methods or the more recent non-deterministic optimization methods (Edgar and Himmelblau, 1988; Nocedal and Wright, 1999; Goldberg, 1989; Kennedy and Eberhart, 2001). It is important to emphasize that Eq. (5) does not restrict any of the conclusions obtained here and that other objective functions can certainly be used for parameter estimation.

After minimization of the objective function, the significance of parameter estimates can be characterized through the covariance matrix defined as (Bard, 1974):

$$\mathbf{V}_{\boldsymbol{\theta}} = \left[\sum_{i=1}^{\text{NE}} \mathbf{B}_i^{\text{T}} \mathbf{V}_i^{-1} \mathbf{B}_i\right]^{-1} \tag{6}$$

which assumes that the model equations may be linearized at the optimum parameter estimates. $\mathbf{B}_i$ is the sensitivity matrix of model responses with respect to the model parameters at the experimental condition i and is defined as

$$\mathbf{B}_i = \begin{bmatrix} \frac{\partial y_{1,i}}{\partial \theta_1} & \cdots & \frac{\partial y_{1,i}}{\partial \theta_1} \\ \vdots & \ddots & \vdots \\ \frac{\partial y_{NY,i}}{\partial \theta_1} & \cdots & \frac{\partial y_{NY,i}}{\partial \theta_{\text{NP}}} \end{bmatrix} \tag{7}$$

where NP is the number of model parameters and NY is the number of model responses.

For single response models, when the covariance matrix of experimental observations is unknown, the parameter estimation is normally performed through minimization of the least squares function:

$$S(\boldsymbol{\theta}) = \sum_{i=1}^{\text{NE}} [y_i^e - y_i^m(\mathbf{x}_i, \boldsymbol{\theta})]^2 \tag{8}$$

If the model is assumed to be perfect, the residuals can be used to determine the variance of experimental observations s^2 (Draper and Smith, 1998) as follows:

$$s^2 = S(\hat{\boldsymbol{\theta}}) / (\text{NE} - \text{NP}) \tag{9}$$

where $S(\hat{\boldsymbol{\theta}})$ is the minimum value of the least squares function (Eq. (8)). The covariance matrix of parameter estimates can then be written as

$$\mathbf{V}_{\boldsymbol{\theta}} = s^2 \left[\sum_{i=1}^{\text{NE}} \mathbf{B}_i^{\text{T}} \mathbf{B}_i\right]^{-1} \tag{10}$$

The main diagonal of the covariance matrix contains the variances of the parameter estimates. These values can be readily used for evaluation of parameter confidence intervals. For instance, the relative error of the parameter estimates can be computed as

$$\text{er}_{\theta_i} = \frac{t_{\text{NE}-\text{NP}}^{(1+\alpha)/2} \sqrt{v_{ii}}}{\theta_i} \tag{11}$$

where $t_{NE-NP}^{(1+\alpha)/2}$ is the t-Student distribution value with a confidence level of α (always equal to 0.95 in this work) and NE − NP degrees of freedom, and v_{ii} is the diagonal element of the covariance matrix that represents the variance of the parameter θ_i.

The off-diagonal elements characterize the covariance between pairs of parameters, which is a measure of the dependence between the parameter estimates. In order to normalize the extent of this dependence, the correlation matrix of parameter estimates should be calculated from the covariance matrix of parameter estimates as

$$\rho_{ij} = \frac{v_{ij}}{\sqrt{v_{ii}v_{jj}}} \tag{12}$$

where v_{ij} is the element ij of the covariance matrix of parameter estimates. The values of all ρ_{ij} are in the range $[-1, 1]$. As the absolute values of ρ_{ij} get closer to 1, the parameters become more correlated and the parameter estimation becomes poorer. The high correlation between parameter estimates can be originated from different reasons, such as the inappropriate model representation and a bad experimental design.

Based on the covariance matrix of parameter estimates, the confidence region of the parameter estimates can be defined as a hyper-ellipsoid in the parameter space. However, due to model nonlinearity, the elliptic approximation can be very poor sometimes, since the real confidence region can present very complex shapes (Donaldson and Schnabel, 1987; Schwaab et al., 2008). The use of reparameterization techniques can improve the elliptical approximation of the confidence regions (Watts, 1994), making the evaluation of the significance of the parameter estimates much easier.

3. The optimum reference temperature

Although reference temperatures are commonly inserted into the Arrhenius equation to reduce the correlation between model parameters, little attention has been given to definition of the best values for the reference temperatures for maximum reduction of correlations. In most cases, the reference temperature is defined as a suitable average of temperature values in the analyzed experimental range.

Schwaab and Pinto (2007) showed that it is possible to determine an optimum reference temperature in order to eliminate parameter correlation and minimize the relative errors of model parameters in models containing a single kinetic constant. However, for models containing more than one kinetic constant, the number of parameter correlations is larger than the reference temperatures that can be defined and it cannot be guarantee that all correlation can be eliminated simultaneously. Besides, the reference temperatures used in the distinct Arrhenius equation should not necessarily be the same.

In these cases, it may be necessary to define a norm for the parameter correlation matrix that takes into account the degree of correlation between each pair of parameters. Definition of reference temperatures should then minimize the proposed norm in order to allow for minimization of parameters correlation. Independently of the selected norm, the procedure consists in searching the reference temperature values that minimize the correlation measure, according with the procedure illustrated in Fig. 1.

Initial guesses must be provided for the reference temperatures values. For instance, initial guesses may be the average temperature values in the analyzed experimental range. Then, estimation of model parameters must be performed with the help of an adequate numerical procedure (Schwaab et al., 2008). As the model performance is not affected by the reparameterization, the optimization of the reference temperatures can be performed without disturbing the optimum model predictions. Although parameter values change, no re-estimation of model parameters is necessary. As the parameter values are known for certain reference temperatures (for instance, the initial guesses), the parameter values can be readily calculated

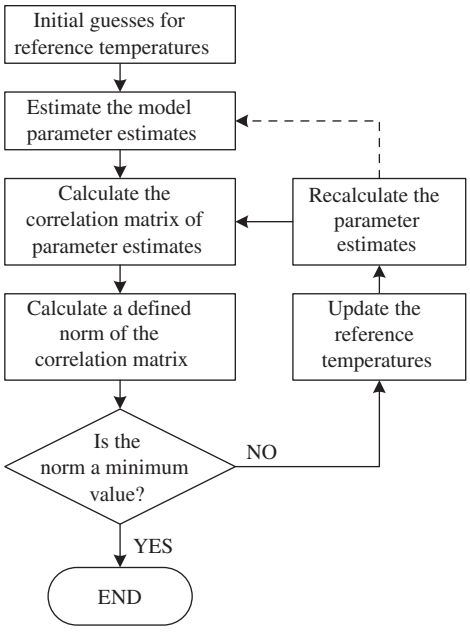

Fig. 1. Schematic representation of the two-step parameter estimation procedure with optimization of reference temperatures.

at any other reference temperature. For instance, if the parameter estimates A^* and B^* are obtained for an initial guess of the reference temperature T_{ref}^*, according to Eq. (2d) the parameter estimates A and B for a new reference temperature T_{ref} become:

$$A = A^* + B - B^* \tag{13a}$$

$$B = \frac{B^* T_{ref}^*}{T_{ref}} \tag{13b}$$

From Eqs. (13a) and (13b) one can write $\boldsymbol{\theta} = \mathbf{g}(\boldsymbol{\theta}^*)$. The covariance matrix, $\mathbf{V}$, of the parameter estimates at the new reference temperature values can be calculated as (Rimensberger and Rippin, 1986)

$$\mathbf{V} = \mathbf{G}^{\mathrm{T}}\mathbf{V}^*\mathbf{G} \tag{14a}$$

where $\mathbf{V}^*$ is the covariance matrix of parameter estimates $\boldsymbol{\theta}^*$ with the reference temperature equal to T_{ref}^* and $\mathbf{G}$ is a NP × NP matrix defined as:

$$\mathbf{G} = \begin{bmatrix} \frac{\partial g_1}{\partial \theta_1^*} & \frac{\partial g_2}{\partial \theta_1^*} & \cdots & \frac{\partial g_{NP}}{\partial \theta_1^*} \\ \frac{\partial g_1}{\partial \theta_2^*} & \frac{\partial g_2}{\partial \theta_2^*} & \cdots & \frac{\partial g_{NP}}{\partial \theta_2^*} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial g_1}{\partial \theta_{NP}^*} & \frac{\partial g_2}{\partial \theta_{NP}^*} & \cdots & \frac{\partial g_{NP}}{\partial \theta_{NP}^*} \end{bmatrix} \tag{14b}$$

Consequently, the recalculation of the covariance matrix of parameter estimates when the reference temperature is changed does not require any additional model computation, which means that the additional computational effort is very small.

Unfortunately, due to the existence of high correlations among model parameters, the parameter estimation may be sometimes very hard, so that the numerical procedure used for minimization of the objective function can be unable to locate the correct optimum parameter estimates. In this case, the parameter estimation procedure should be performed iteratively, as indicated by the dashed line of Fig. 1.

As discussed above, when the problem involves more than one Arrhenius equation, it is necessary to define some norm for the correlation matrix of parameter estimates for optimization of reference temperatures. After estimation of model parameters using the guesses for all T_{ref}, the second step consists in minimizing the proposed norm of the correlation matrix of parameter estimates through manipulation of reference temperatures. The simplest norm that can be defined is the sum of the squares of all parameter correlations, computed in accordance with the following equation:

$$F_1 = \sum_{i=1}^{\mathrm{NP}-1} \sum_{j=i+1}^{\mathrm{NP}} \rho_{ij}^2 \tag{15}$$

The norm defined in Eq. (15) is empirical. Other similar norms can be proposed, such as the sum of the absolute values of the parameter correlations. Besides, if one is interested in reducing a particular set of parameter correlations, Eq. (15) can be readily modified in order to take into account only the selected set of parameter correlations. The norm in Eq. (15) can be related to the experimental design criterion proposed by Pritchard and Bacon (1978), where new experiments could be designed for reduction of the correlations among model parameters.

A norm can be developed with the use of the characteristic values of the parameter correlation matrix. When the shape of the confidence region is spherical, the characteristic values of the parameter correlation matrix are equal and the effects of parameter correlations can be minimized. As the parameter correlation matrix is positive definite, all the characteristic values are positive. Then, the optimization of the reference temperatures can be performed in order to make the characteristic values as equal as possible, according to:

$$F_2 = \sum_{i=1}^{\mathrm{NP}} \left(1 - \frac{\lambda_i}{\lambda_{\max}}\right) \tag{16}$$

where λ_i is the characteristic value and $\lambda_{\max}$ is the maximum characteristic value. When the ratios between the characteristic values $\lambda_i/\lambda_{\max}$ get close to 1, the function F_2 defined in Eq. (16) approaches 0 and F_2 is minimized. The norm defined in Eq. (16) is related to the shape criterion used for experimental design for reduction of parameter correlation, as proposed by Hosten (1974).

The characteristic vectors of the correlation matrix of parameter estimates can be used for definition of the norm

$$F_3 = \sum_{i=1}^{\mathrm{NP}} (1 - \mu_{i,\max}^2) \tag{17}$$

where $\mu_{i,\max}$ is the component of the ith characteristic vector with largest absolute value. The minimization of the norm defined in Eq. (17) makes the largest components of the distinct characteristic vectors close to 1. As a consequence, the characteristic vectors become aligned to the main parameter axis, reducing the correlation among the parameters.

Although the three norms described in Eqs. (15)–(17) are intended to minimize the correlations among the parameter estimates, these norms do not lead necessarily to the same solution, which means that the optimum reference temperatures may be different, depending on the used norm as illustrated in the next section. It is also important to emphasize that other norms can be defined and used for definition of the reference temperatures, in accordance with the proposed two-step parameter estimation procedure.

4. Examples

In the first example the parameter estimation of a multilinear model is discussed. It is shown theoretically and numerically in this simple case that it is not possible to eliminate all correlations with the proposed reparameterization scheme. The second example deals with a catalytic rate model, usually found in chemical kinetics. The third example describes the estimation of parameters in temperature programmed desorption experiments.

As in the previous work of Schwaab and Pinto (2007), minimization of the objective function during the parameter estimation procedure is performed with a hybrid method. The search is initiated with the particle swarm optimization method (Kennedy and Eberhart, 1995, 2001), a non-deterministic method which performs a global search in order to locate the global minimum and provide the likelihood confidence region of parameter estimates (Schwaab et al., 2008). The best point located by the particle swarm optimization is then used as the initial guess for a Gauss–Newton based procedure (Noronha et al., 1993), which assures the precision of the final point estimate and provides the covariance matrix of parameter estimates, used for evaluation of the ellipsoidal confidence region and for calculation of the norm of the correlation matrix of parameter estimates. The optimization of the reference temperatures was also performed with the particle swarm optimization method, due to its capabilities for solving complex (multiple minima and nonconvex) problems. Since the recalculation of the covariance matrix of parameter estimates is performed with the help of Eqs. (14a) and (14b) and does not require any model solution, the additional computer time required for optimization of reference temperature values is very small. In the examples analyzed here, it never took more than 15 s to perform the reference temperature optimization step. The algorithms and model implementations were done in FORTRAN, in a personal desktop computer (Pentium 4 equipped with a 3.0 MHz processor and 1024 Mb of RAM memory).

4.1. Example 1—a multilinear model

Let a valid model be described as

$$y = \alpha_0 + \alpha_1 x_1 + \cdots + \alpha_{NX} x_{NX} \tag{18}$$

where x_j ($j = 1, \ldots, NX$) are the independent variables, α_j ($j = 0, \ldots, NX$) are the model parameters and y is the model response (or the dependent variable). With an available experimental data set defined as $(x_{1,i}^e, \ldots, x_{n,i}^e, y_i^e)$, with $i = 1, \ldots, \mathrm{NE}$, the maximum likelihood estimation of the parameters can be defined as the parameters values that minimize the objective function:

$$S(\boldsymbol{\alpha}) = \sum_{i=1}^{\mathrm{NE}} [y_i^e - y_i^m(\mathbf{x}_i, \boldsymbol{\alpha})]^{\mathrm{T}} \mathbf{V}_i^{-1} [y_i^e - y_i^m(\mathbf{x}_i, \boldsymbol{\alpha})] \tag{19}$$

where $\boldsymbol{\alpha}$ is the vector of model parameters, $\mathbf{y}^e = [y_1^e, y_2^e, \ldots, y_{\mathrm{NE}}^e]^{\mathrm{T}}$ is the vector of experimental values and $\mathbf{y}^m = [y_1^m, y_2^m, \ldots, y_{\mathrm{NE}}^m]^{\mathrm{T}}$ is the vector of model responses, given by Eq. (18), $\mathbf{V}_y$ is the matrix of experimental variances and S is the objective function to be minimized with respect to the parameters $\boldsymbol{\alpha}$. This parameter estimation problem presents an analytical solution, defined as:

$$\boldsymbol{\alpha} = (\mathbf{X}^{\mathrm{T}} \mathbf{V}_{\mathbf{y}}^{-1} \mathbf{X})^{-1} \mathbf{X}^{\mathrm{T}} \mathbf{V}_{\mathbf{y}}^{-1} \mathbf{y}^e \tag{20}$$

$$\mathbf{V}_{\boldsymbol{\alpha}} = (\mathbf{X}^{\mathrm{T}} \mathbf{V}_{\mathbf{y}}^{-1} \mathbf{X})^{-1} \tag{21}$$

where $\mathbf{X} = [1 \vdots \mathbf{x}_1^e \vdots \mathbf{x}_2^e \vdots \cdots \vdots \mathbf{x}_{NX}^e]$ is a matrix of experimental data of the independent variables and $\mathbf{V}_{\boldsymbol{\alpha}}$ is the covariance matrix of parameter estimates, defined in Eq. (6) for a general case. Depending on the nature of the available experimental data, $\mathbf{V}_{\boldsymbol{\alpha}}$ can be a full matrix. In other words, the element ij of $\mathbf{V}_{\boldsymbol{\alpha}}$ is not null, indicating that parameters α_i and α_j are correlated to some extent.

If the model described in Eq. (18) is reparameterized in the form

$$y = \beta_0 + \beta_1(x_1 - x_1^r) + \cdots + \beta_{NX}(x_{NX} - x_{NX}^r) \tag{22}$$

where $(x_1^r, \ldots, x_{NX}^r)$ are arbitrarily defined reference values, then it is clear that

$$\alpha_0 = \beta_0 + \beta_1 x_1^r + \cdots + \beta_{NX} x_{NX}^r \tag{23}$$

$$\alpha_i = \beta_i, \quad i = 1, \ldots, NX \tag{24}$$

In this case, the solution of the parameter estimation problem is

$$\boldsymbol{\beta} = [(\mathbf{X} - \mathbf{X}^r)^{\mathrm{T}} \mathbf{V}_{\mathbf{y}}^{-1} (\mathbf{X} - \mathbf{X}^r)]^{-1} (\mathbf{X} - \mathbf{X}^r)^{\mathrm{T}} \mathbf{V}_{\mathbf{y}}^{-1} \mathbf{y}^e \tag{25}$$

$$\mathbf{V}_{\boldsymbol{\beta}} = [(\mathbf{X} - \mathbf{X}^r)^{\mathrm{T}} \mathbf{V}_{\mathbf{y}}^{-1} (\mathbf{X} - \mathbf{X}^r)]^{-1} \tag{26}$$

where $\mathbf{X}^r = [1 \vdots \mathbf{x}_1^r \vdots \mathbf{x}_2^r \vdots \cdots \vdots \mathbf{x}_{NX}^r]$ is a constant matrix that contains the reference values. If $\mathbf{V}_y$ is diagonal (independent experiments) then the elements of $\mathbf{V}_{\boldsymbol{\beta}}^{-1}$ can be written in the form

$$[v_{\boldsymbol{\beta}}]_{ij}^{-1} = \sum_{n=1}^{\mathrm{NE}} \frac{(x_{in} - x_i^r)(x_{jn} - x_j^r)}{\sigma_n^2} \tag{27}$$

As $x_0^r = 0$ and $x_{0n} = 1$, then

$$[v_{\boldsymbol{\beta}}]_{0j}^{-1} = \sum_{n=1}^{\mathrm{NE}} \frac{(x_{jn} - x_j^r)}{\sigma_n^2} \tag{28}$$

The elements defined in Eq. (28) can be nullified if

$$x_j^r = \frac{\sum_{n=1}^{\mathrm{NE}} x_{jn}/\sigma_n^2}{\sum_{n=1}^{\mathrm{NE}} 1/\sigma_n^2} \tag{29}$$

Inserting Eq. (29) into Eq. (27), it is possible to write

$$[v_{\boldsymbol{\beta}}]_{ij}^{-1} = \sum_{n=1}^{\mathrm{NE}} \frac{1}{\sigma_n^2} \left(x_{in} - \frac{\sum_{m=1}^{\mathrm{NE}} x_{im}/\sigma_m^2}{\sum_{m=1}^{\mathrm{NE}} 1/\sigma_m^2} \right) \times \left(x_{jn} - \frac{\sum_{m=1}^{\mathrm{NE}} x_{jm}/\sigma_m^2}{\sum_{m=1}^{\mathrm{NE}} 1/\sigma_m^2} \right) \tag{30}$$

And after some algebraic manipulation

$$[v_{\boldsymbol{\beta}}]_{ij}^{-1} = \sum_{n=1}^{\mathrm{NE}} \frac{x_{in} x_{jn}}{\sigma_n^2} - x_i^r x_j^r \sum_{n=1}^{\mathrm{NE}} \frac{1}{\sigma_n^2} \tag{31}$$

which cannot be made equal to zero for general arbitrary sets of experimental data. (This difficulty can certainly be overcome with the help of experimental design techniques.) For instance, let us assume that the experimental data are available as presented in Table 1.

Therefore,

$$\mathbf{X} = \begin{bmatrix} 1 & -1 & -1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \\ 1 & 0 & 0 \end{bmatrix} \tag{32}$$

Table 1
Experimental data for Example 1

x_1^e	x_2^e	y^e	σ_e^2
−1	−1	−1	1
−1	1	1	2
1	−1	1	3
0	0	1	4

$$\mathbf{y}^e = [-1 \;\; 1 \;\; 1 \;\; 1]^{\mathrm{T}} \tag{33}$$

$$\mathbf{V}_{\mathbf{y}} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 4 \end{bmatrix} \tag{34}$$

Using Eqs. (20) and (21) one can obtain

$$\boldsymbol{\alpha} = [1 \;\; 1 \;\; 1]^{\mathrm{T}} \tag{35}$$

$$\mathbf{V}_{\boldsymbol{\alpha}} = \begin{bmatrix} 0.95 & 0.57 & 0.38 \\ 0.57 & 0.89 & 0.18 \\ 0.38 & 0.18 & 0.70 \end{bmatrix} \tag{36}$$

The covariance matrix of parameter estimates is a full matrix, which means that model parameters are correlated to some extent, as can be easier observed in the correlation matrix of parameter estimates

$$\mathbf{R}_{\boldsymbol{\alpha}} = \begin{bmatrix} 1.00 & 0.62 & 0.47 \\ 0.62 & 1.00 & 0.23 \\ 0.47 & 0.23 & 1.00 \end{bmatrix} \tag{37}$$

Eq. (37) shows that the parameters are correlated at some degree. Using Eq. (29), the reference values for the variable can be calculated in order to eliminate the parameter correlations and the matrix $\mathbf{X}^r$ can be defined as

$$\mathbf{X}^r = \begin{bmatrix} 0 & -0.56 & -0.40 \\ 0 & -0.56 & -0.40 \\ 0 & -0.56 & -0.40 \\ 0 & -0.56 & -0.40 \end{bmatrix} \tag{38}$$

Now, using Eqs. (25) and (26) one can obtain

$$\boldsymbol{\beta} = [1/25 \;\; 1 \;\; 1]^{\mathrm{T}} \tag{39}$$

$$\mathbf{V}_{\boldsymbol{\beta}} = \begin{bmatrix} 0.48 & 0.00 & 0.00 \\ 0.00 & 0.89 & 0.18 \\ 0.00 & 0.18 & 0.70 \end{bmatrix} \tag{40}$$

With the reparameterization of the model equation, the covariance matrix is not completely full and the calculation of the parameter correlation matrix gives

$$\mathbf{R}_{\boldsymbol{\beta}} = \begin{bmatrix} 1.00 & 0.00 & 0.00 \\ 0.00 & 1.00 & 0.23 \\ 0.00 & 0.23 & 1.00 \end{bmatrix} \tag{41}$$

Eq. (41) shows that the correlations between the parameters β_1 and β_2 and between the parameters β_1 and β_3 were eliminated. The correlation between the parameters β_2 and β_3 was not affected by the reparameterization. This clearly shows that it is not possible to eliminate all parameter correlations when the number of parameter correlations is larger than the number of reparameterization variables (the reference values).

In order to minimize the parameter correlation, it is necessary to manipulate the reference values in order to minimize a suitable norm of $\mathbf{V}_{\beta}$. This example shows that all the parameter correlations cannot be made equal to zero simultaneously without the help of experimental design techniques even when the model is linear. This shows that some sort of numerical procedure must be implemented for minimization of parameter correlations in multi-parameter models, as proposed in this work.

4.2. Example 2—-catalytic kinetic model

In this example the experimental data for *o*-xylene oxidation obtained by J.A. Jussola (reported in Bates and Watts, 1988) is considered (the experimental data are presented in the Appendix). Available data include the reaction rates (r in mol/($\mathrm{mol_{cat}}$ s)) as

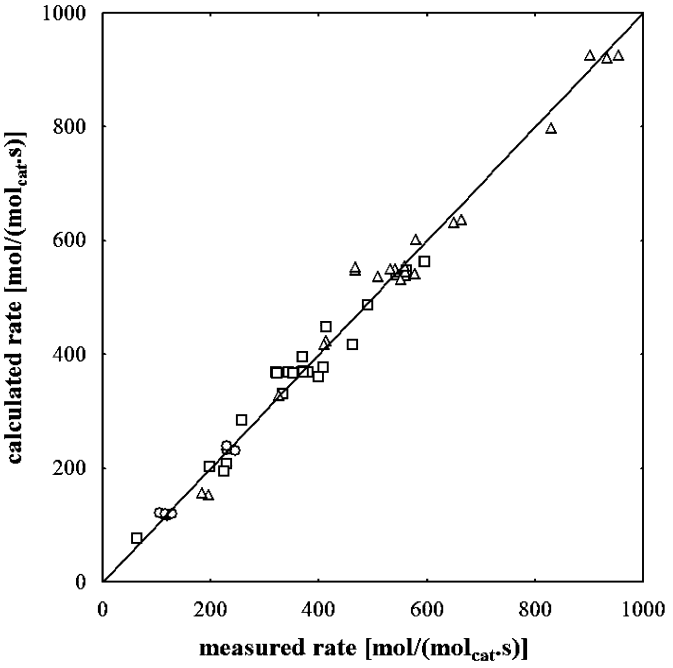

Fig. 2. Model fit to the experimental values in Example 2 (○: 543 K; □: 563 K; △: 573 K).

Table 2
Parameter estimation results with traditional Arrhenius equation in Example 2

Parameter	Estimated value	Relative error (%)
A_1	44.96	7.676
A_2	28.67	26.65
B_1 (kJ/mol)	153.1	10.61
B_2 (kJ/mol)	60.55	59.63

functions of the oxygen and xylene concentrations (C_O and C_X, both in mol/L) and temperature. The proposed model is

$$r = \frac{k_1 k_2 C_O C_X}{k_1 C_O + n k_2 C_X} \tag{42}$$

where n is the stoichiometric number (equal to 2.2788) and k_i is the kinetic constant defined in accordance with the Arrhenius equation as

$$k_i = \exp\left[A_i + B_i\left(\frac{T - T_{\mathrm{ref},i}}{T}\right)\right] \tag{43}$$

where $T_{\mathrm{ref},i}$ is the reference temperature of the kinetic constant k_i. For the sake of comparison, the parameter estimation was performed first without using the reference temperature, writing the traditional Arrhenius equation as

$$k_i = \exp(A_i - B_i/RT) \tag{44}$$

The quality of the model fit to the experimental data is presented in Fig. 2. It must be stated that the model fit is independent of the reparameterization, so that the quality of the model adjustment is the same for all parameterizations used in this example. The minimum value attained for the objective function was equal to 40371.3. The estimated parameters and respective relative errors (computed in accordance with Eq. (11)) obtained are presented in Table 2. Table 3 presents the correlation matrix of the parameter estimates.

As Table 3 shows, some parameter correlations are very high. For the pairs of parameters A_1–E_1 and A_2–E_2 the correlation values are practically equal to 1 (given the number of decimal digits).

Table 3
Parameter correlation matrix with traditional Arrhenius equation in Example 2

	A_1	A_2	B_1	B_2
A_1	1.00	−0.80	1.00	−0.79
A_2	−0.80	1.00	−0.80	1.00
B_1	1.00	−0.80	1.00	−0.79
B_2	−0.79	1.00	−0.79	1.00

Table 4
Parameter estimation results in Example 2 with the reference temperatures equal to: $T_{\mathrm{ref}1} = T_{\mathrm{ref}2} = 558$ K

Parameter	Estimated value	Relative error (%)
A_1	11.95	0.672
A_2	15.62	1.145
B_1	33.00	10.61
B_2	13.05	59.63

Table 5
Parameter correlation matrix in Example 2 with the reference temperatures equal to: $T_{\mathrm{ref}1} = T_{\mathrm{ref}2} = 558$ K

	A_1	A_2	B_1	B_2
A_1	1.00	−0.79	−0.69	0.58
A_2	−0.79	1.00	0.54	−0.79
B_1	−0.69	0.54	1.00	−0.79
B_2	0.58	−0.79	−0.79	1.00

Table 6
Parameter estimation results in Example 2 with the optimized reference temperatures using Eq. (15): $T_{\mathrm{ref}1} = 565.6$ K; $T_{\mathrm{ref}2} = 568.2$ K

Parameter	Estimated value	Relative error (%)
A_1	12.39	0.452
A_2	15.85	0.695
B_1	32.56	10.61
B_2	12.82	59.63

In order to minimize the parameter correlations, the procedure described in Fig. 1 was used. The initial values of the reference temperatures were set equal to 558 K (the average temperature value of the experimental range). The model fit to the experimental data is presented in Fig. 2 and the parameter estimation results obtained with these reference temperatures are shown in Tables 4 and 5.

Table 4 shows that the use of reference temperatures of 558 K reduces significantly the relative error for parameters A_1 and A_2. However, the relative errors of parameters B_1 and B_2 (related to the parameters E_1 and E_2) are not affected by the reparameterization. Similar results were observed by Schwaab and Pinto (2007) when models with only one kinetic constant were considered. The parameter correlations presented in Table 5 are also smaller than the ones presented in Table 3.

Starting from the results obtained with the references temperatures of 558 K, minimizations of the norms of the parameter correlation matrix were performed. After minimization of the norm defined in Eq. (15), the optimum references temperatures were equal to $T_{\mathrm{ref}1} = 565.6$ K and $T_{\mathrm{ref}2} = 568.2$ K. These values are slightly higher than the average temperature value of the experimental range. The results obtained after parameter estimation with these optimized reference temperatures are presented in Tables 6 and 7. In Fig. 3 the shape of the Norm 1 (Eq. (15)) as a function of the reference temperatures is presented as a contour plot.

Table 6 shows that the relative errors of parameters A_1 and A_2 are smaller than the ones presented in Table 4. Again, the relative errors of parameters B_1 and B_2 were not affected by reparameterization, as observed by Schwaab and Pinto (2007). Table 7 shows that the optimization of the references temperatures with the norm defined

Table 7
Parameter correlation matrix in Example 2 with the optimized reference temperatures using Eq. (15): $T_{ref1} = 565.6\,K$; $T_{ref2} = 568.2\,K$

	A_1	A_2	B_1	B_2
A_1	1.00	−0.87	−0.10	0.13
A_2	−0.87	1.00	−0.14	−0.01
B_1	−0.10	−0.14	1.00	−0.79
B_2	0.13	−0.01	−0.79	1.00

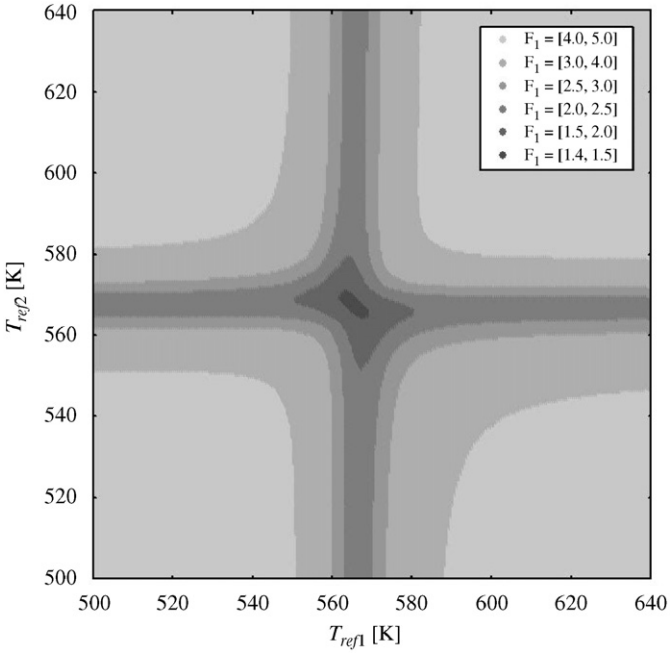

Fig. 3. Norm 1 as a function of T_{ref1} and T_{ref2} in Example 2.

Table 8
Parameter estimation results in Example 2 with the optimized reference temperatures using Eq. (16): $T_{ref1} = 565.3\,K$; $T_{ref2} = 569.0\,K$

Parameter	Estimated value	Relative error (%)
A_1	12.38	0.455
A_2	15.87	0.697
B_1	32.58	10.61
B_2	12.80	59.63

in Eq. (15) can reduce the parameter correlation for very low values. The exceptions were the correlations between the parameters B_1 and B_2 and between the parameters A_1 and A_2. Fig. 3 shows that Norm 1 leads to formation of two valleys, with a minimum located at the point where the two valleys cross each other.

The second minimized norm is the one defined in Eq. (16). After minimization of this norm, the optimum references temperatures were equal to $T_{ref1} = 565.3\,K$ and $T_{ref2} = 569.0\,K$. These values are almost the same ones obtained with the first norm (Eq. (15)). The results obtained after parameter estimation using these reference temperatures are shown in Tables 8 and 9. The contour plot of the Norm 2 (Eq. (16)) as a function of the reference temperatures is presented in Fig. 4.

The relative errors and the parameter correlations are slightly worse than the results presented in Tables 6 and 7, despite the correlation between the parameters A_1 and A_2 and the correlation between the parameters B_1 and B_2. It can be seen in Fig. 4 that the shape of the contours of Norm 2 are very similar to the contours of Norm 1 (Fig. 3). Therefore, Norms 1 and 2 lead to very similar results in Example 2.

Table 9
Parameter correlation matrix in Example 2 with the optimized reference temperatures using Eq. (16): $T_{ref1} = 565.3\,K$; $T_{ref2} = 569.0\,K$

	A_1	A_2	B_1	B_2
A_1	1.00	−0.84	−0.14	0.16
A_2	−0.84	1.00	−0.21	0.08
B_1	−0.14	−0.21	1.00	−0.79
B_2	0.16	0.08	−0.79	1.00

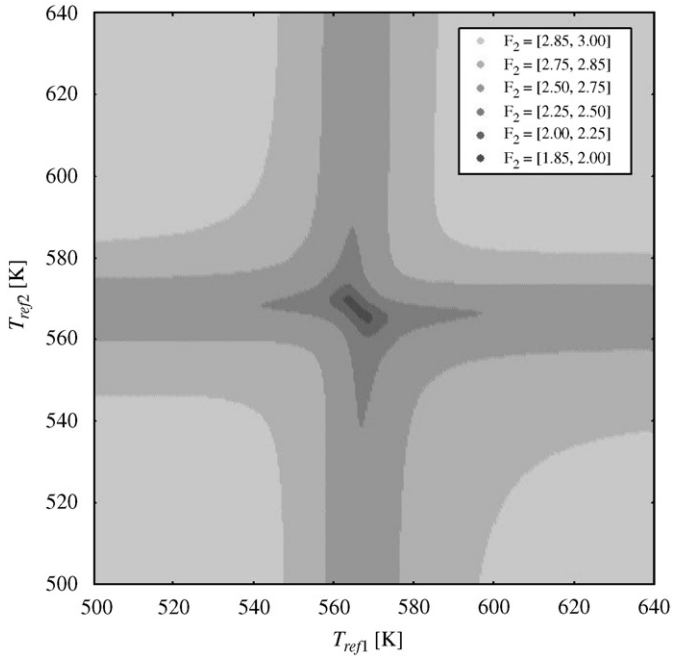

Fig. 4. Norm 2 as a function of T_{ref1} and T_{ref2} in Example 2.

Table 10
Parameter estimation results in Example 2 with the optimized reference temperatures using Eq. (17): $T_{ref1} = 566.6\,K$; $T_{ref2} = 673.0\,K$

Parameter	Value	Error (%)
A_1	12.47	0.447
A_2	16.65	6.691
B_1	32.48	10.61
B_2	12.02	59.63

Table 11
Parameter correlation matrix in Example 2 with the optimized reference temperatures using Eq. (17): $T_{ref1} = 566.6\,K$; $T_{ref2} = 673.0\,K$

	A_1	A_2	B_1	B_2
A_1	1.00	−0.04	0.01	0.04
A_2	−0.04	1.00	−0.80	1.00
B_1	0.01	−0.80	1.00	−0.79
B_2	0.04	1.00	−0.79	1.00

When the third norm defined in Eq. (17) is used for optimization of the reference temperatures, the optimum values obtained were equal to $T_{ref1} = 566.6\,K$ and $T_{ref2} = 673.0\,K$. The value of T_{ref1} was practically the same one obtained for the two previous norms, but the value of T_{ref2} was much higher than the other ones. The results obtained after parameter estimation with these reference temperatures are shown in Tables 10 and 11. Fig. 5 shows the contour plot of Norm 3 (Eq. (17)) as a function of the reference temperatures.

Table 10 shows that the relative error of parameter A_2 was much higher than the values obtained with the two previous norms,

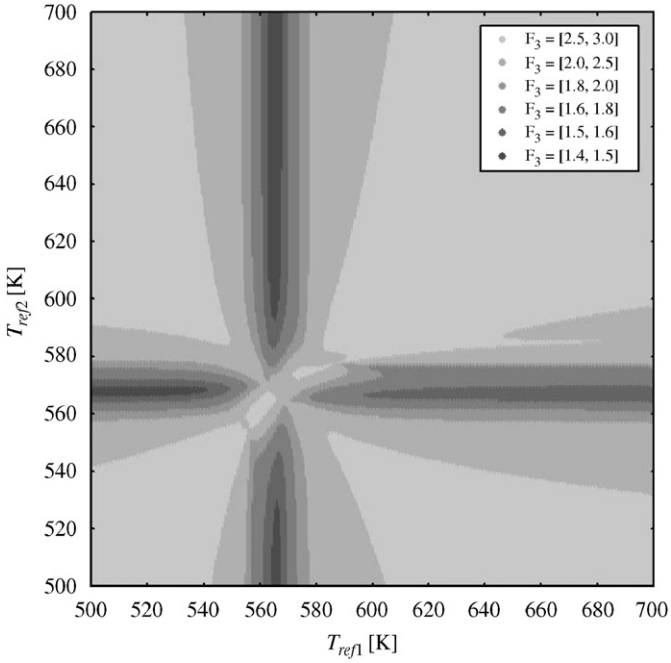

Fig. 5. Norm 3 as a function of T_{ref1} and T_{ref2} in Example 2.

although the relative error of parameter A_1 was slightly smaller. Observing the parameter correlations in Table 11, it becomes clear that this third norm reduces the correlations of parameter A_1, since all correlations between parameter A_1 with the other parameters were very small. However, the correlations between the parameters A_2–B_1 and A_2–B_2 become equal to −0.80 and 1.00 (given the number of decimal digits). Therefore, the optimization of the Norm 3 led to one characteristic vector aligned almost perfectly with one of the parameter axes, although the remaining characteristic vectors were still rotated in respect to the parameter axes.

The complex shape shown in Fig. 5 explains the different results obtained with the Norm 3. For the first two norms, the minimum was placed at the crossing of two valleys. For Norm 3, the equivalent point is a local maximum, as shown in Fig. 5. The global and local minima are placed in the four valleys that are connected by the central point of maximum.

In general, all three norms lead to development of complex shapes. For this reason, difficulties may arise during the optimization of the norms, making the definition of the optimum reference temperatures a hard task. The use of the particle swam optimization method for minimization of the norms can overcome these difficulties due its global character and because derivatives are not necessary.

In order to understand the behavior of the relative errors and the correlations of the parameters, these values were calculated as functions of T_{ref1} and T_{ref2} values. It was observed that the relative errors of parameters B_1 and B_2 do not depend on the references temperatures, as shown by Schwaab and Pinto (2007). Besides, the relative error of parameter A_1 depends only on T_{ref1}, while the relative error of parameter A_2 depends only on T_{ref2}. This is shown in Fig. 6, where it is also shown that the relative errors attain minimum values around specific values of T_{ref}. The relative error of parameter A_1 attains a minimum value of 0.447% at T_{ref1} equal to 567.0 K, while the minimum relative error for A_2 is equal to 0.695% at T_{ref2} equal to 568.5 K.

With respect to the parameter correlations, it was observed that the correlation between the parameters B_1 and B_2 is independent of the adopted reference temperatures. The correlation between the

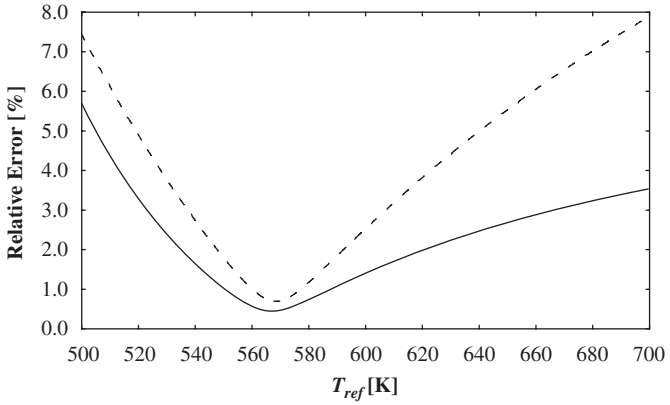

Fig. 6. Relative errors of parameters A_1 (full line) and A_2 (dashed line) as a function of T_{ref1} and T_{ref2}, respectively, in Example 2.

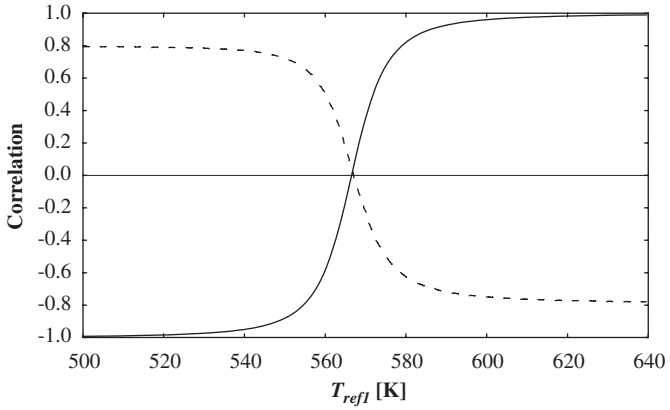

Fig. 7. Correlation between parameters A_1–B_1 (full line) and A_1–B_2 (dashed line) as a function of T_{ref1} in Example 2.

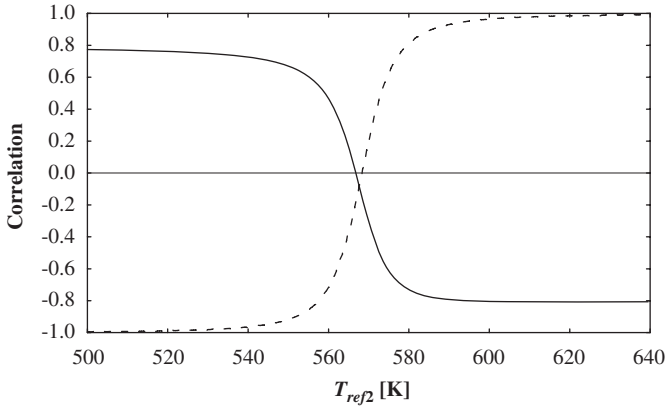

Fig. 8. Correlation between parameters A_2–B_1 (full line) and A_2–B_2 (dashed line) as a function of T_{ref2} in Example 2.

parameters A_1–B_1 and A_1–B_2 depend only on T_{ref1}, while correlations between parameters A_2–B_1 and A_2–B_2 depends on T_{ref2}, as shown in Figs. 7 and 8. It can also be observed that these correlations can be made equal to 0: correlation A_1 and B_1 is null for T_{ref1} equal to 566.8 K; correlation A_1–B_2 is null for T_{ref1} equal to 568.3 K; correlation A_2–B_1 is null for T_{ref2} equal to 566.5 K; correlation A_2–B_2 is null for T_{ref2} equal to 567.0 K. Fortunately, the reference values that lead to null correlations are similar in all cases.

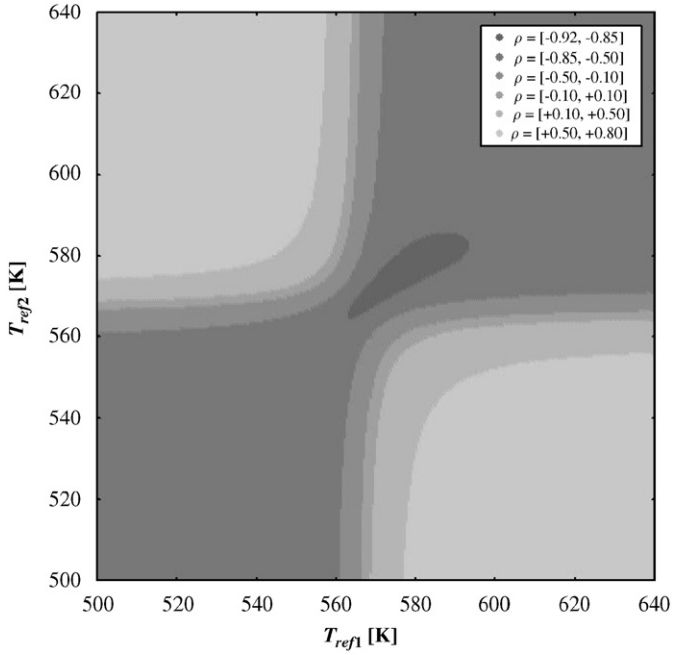

Fig. 9. Correlation between parameters A_1–A_2 as a function of T_{ref1} and T_{ref2} in Example 2.

The correlation between the parameters A_1 and A_2 depends on both T_{ref1} and T_{ref2} in a complex manner, as shown in Fig. 9. It can be seen that the reference temperatures that minimize Norms 1 and 2 (Eqs. (14) and (15)) lead to high correlation between the parameters A_1 and A_2. Besides, the values of the reference temperatures that lead to null A_1–A_2 correlation form a discontinuous curved line, which corresponds to the region in Fig. 9 defined by $\rho = [-0.10, +0.10]$. The correlation between parameters A_1 and A_2 becomes very high at the center of Fig. 9, where temperature reference values allow for elimination of the other parameter correlations, as shown in Figs. 7 and 8. This explains why it is not possible to minimize all the parameter correlations simultaneously and why minimization of the different norms leads to different reference temperatures.

In this example, minimization of Norms 1 and 2 led to similar results, allowing for reduction of all the parameter correlations, despite the high residual correlation between parameters A_1–A_2 and B_1–B_2 (the last one is insensitive to modification of the reference temperature values). Besides, minimization of Norms 1 and 2 also led to parameter estimates with smaller relative errors, improving the confidence and quality of the obtained results. Minimization of Norm 3 did not lead to efficient reduction of correlations, because it was observed that one of the parameters dominated the final value of the norm (in the analyzed case, parameter A_1), while the other correlations remained very high.

4.3. Example 3—TPD model

TPD (temperature-programmed desorption) is an experimental method used to characterize solid surfaces, commonly used for characterization of catalyst active sites in solid catalysis (Kanervo et al., 2006; Resende et al., 2006). According to the TPD procedure, a gaseous component is first adsorbed by the solid at controlled temperature until saturation in a vessel that contains the catalyst. Subsequently, an inert gas stream is passed through the vessel while the temperature is increased linearly. As a consequence, the adsorbed gas is desorbed. The shape of the obtained desorption profile depends on the existence of distinct adsorption sites with distinct adsorptions energies, frequently presenting multiple peaks.

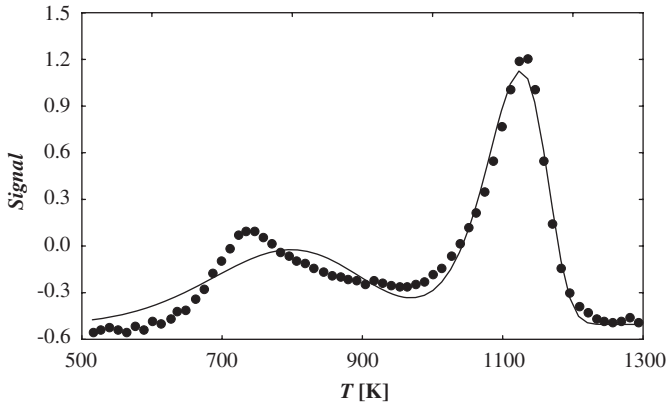

Fig. 10. Model fit (line) to the experimental values (points) in Example 3.

A mathematical model is proposed here to describe a TPD experiment. It is assumed that the number of adsorption sites is constant during the experiment, that desorption enthalpy does not vary significantly along the test, that readsorption and surface diffusion of the adsorbate are negligible and that desorption rates follow a first-order kinetics. Under these assumptions, the mass balance of adsorbed molecules in the catalyst site i can be expressed as

$$\frac{dN_i}{dt} = -k_i N_i, \quad N_i(0) = N_{i0} \tag{45}$$

where N_i is the normalized number of active sites of type i containing an adsorbed molecule (N_{i0} is its initial value) and k_i is the desorption rate constant. Temperature dependence of k_i is assumed to follow the Arrhenius equation (Eq. (43)). The total rate of desorption (R) can then be written as

$$R = \sum_{i=1}^{NS} k_i N_i \tag{46}$$

where NS is the number of distinct site types. The obtained experimental measurement is an electric signal that is proportional to the adsorbate concentration in the gas stream. For this reason, this signal is considered to obey the following relation:

$$\text{Signal} = a_1(R - R_{ref}) + a_0 \tag{47}$$

where a_1 and a_0 are parameters to be estimated and R_{ref} is a reference rate value used to minimize the correlation between the parameters a_1 and a_0. The estimation of a_1 and a_0 from the TPD data is equivalent to the in-situ calibration of the detector setup.

The experimental data presented in this example represent the desorption of ammonia from a hydroxyapatite catalyst (Resende et al., 2006). (Experimental details are omitted because they are not relevant for the purposes of the presented paper). The rate of temperature increase was equal to 15 K/min and the initial temperature was equal to 343 K. The number of distinct active sites in the catalyst was assumed to be equal to two, meaning that, the number of parameters to be estimated was equal to 7: A_1, B_1, A_2, B_2, a_0, a_1 and N_{10} (observe that the initial number of the second type of active sites can be calculated as $N_{20} = 1 - N_{10}$).

The experimental data and the quality of the model fit are presented in Fig. 10. The minimum value for the objective function was equal to 0.496, independently of the adopted reparameterization. Fig. 10 indicates that improvement can be obtained with inclusion of an additional catalyst site and/or modification of the rate expressions. This is not pursued here because improvement of the model fit is unimportant for the purposes of the present manuscript.

Table 12
Used reference values in Example 3

	Traditional Arrhenius	Initial guess	Norm 1	Norm 2	Norm 3
T_{ref1} [K]	∞	900.0	717.51	718.75	772.97
T_{ref2} [K]	∞	900.0	1093.1	1058.5	1094.6
$R_{ref} \times 10^4$	0.0000	0.0000	2.9128	2.9144	2.9214

Table 13
Estimated parameter values in Example 3

Parameter	Traditional Arrhenius	Initial guess	Norm 1	Norm 2	Norm 3
A_1	0.2582	−5.473	−6.930	−6.917	−6.414
B_1	42.88	5.727	7.186	7.174	6.671
A_2	20.30	−11.55	−5.924	−6.781	−5.887
B_2	238.3	31.84	26.23	27.09	26.182
a_1	1246	1246	1246	1245	1246
a_0	−0.5038	−0.5040	−0.1410	−0.1408	−0.1400
N_{10}	0.4141	0.4143	0.4142	0.4142	0.4142

Table 14
Relative parameter errors (%) in Example 3

Parameter	Traditional Arrhenius	Initial guess	Norm 1	Norm 2	Norm 3
A_1	590.4	6.0	2.1	2.1	2.7
B_1	21.3	21.3	21.3	21.3	21.3
A_2	10.0	3.8	1.1	1.4	1.1
B_2	7.7	7.7	7.7	7.7	7.7
a_1	11.4	11.4	11.3	11.3	11.4
a_0	9.2	9.2	15.0	15.1	15.1
N_{10}	10.9	10.9	10.9	10.9	10.9

In this example five different reparameterizations were used for the kinetic constant. The first one was the traditional Arrhenius equation (Eq. (43); that is, without reparameterization). The second one was the reparameterized Arrhenius equation (Eq. (43)) with the temperature reference values fixed at 900 K (approximately the mid-point temperature, as shown in Fig. 10) and the reference rate value set equal to 0.0. These values were also used as initial guesses for the optimization of the reference values in the second step of the proposed two-step estimation algorithm. The other three reparameterizations correspond to the optimized values obtained after minimization of Norms 1–3 (Eqs. (15)–(17)). These optimum reference values are shown in Table 12. The estimated parameter values and the relative parameter errors are presented in Tables 13 and 14, respectively.

As shown in Table 14, the relative errors of parameters B_1, B_2, a_1 and N_{10} are independent of the adopted reference values. The relative errors of parameters A_1 and A_2 are reduced very significantly after the reparameterization. However, the relative error of parameter a_0 increased when a reference rate value R_{ref} different from 0 were used, due to the reduction of the parameter estimate (from −0.50 to −0.14).

As observed previously, the parameter correlations decreased very significantly after the reparameterization, as shown in Tables 15–19. Once more, the parameter correlations between pairs of parameters B_1, B_2, a_1 and N_{10} are independent of the adopted reference values. When the traditional Arrhenius equation was used (Table 15), the parameter correlations were generically high, especially for parameters A_1–B_1 and A_2–B_2. This means that the kinetics of desorption cannot be analyzed properly with the proposed model. As shown in Table 16, the situation cannot be improved through definition of the reference values based solely on the range of analyzed temperatures.

When the reference values were optimized, very small values for the correlations were obtained (although some of the correlations are independent of the adopted reference values). When minimization of Norm 1 (Table 17) was performed, the parameter correlations were very small and comparable to the values obtained through minimization of Norm 2 (Table 18). The only significant difference was observed for parameter correlation between A_2 and B_2: the correlation was equal to −0.04 in the first case and equal to −0.73 in the second case. The optimized reference values obtained after minimization of Norm 3 (Table 19) also led to low parameter

Table 15
Parameter correlation matrix in Example 3 with traditional Arrhenius equation

	A_1	B_1	A_2	B_2	a_1	a_0	N_{10}
A_1	1.00	1.00	−0.03	−0.04	−0.63	0.56	−0.74
B_1	1.00	1.00	−0.01	−0.02	−0.63	0.56	−0.72
A_2	−0.03	−0.01	1.00	1.00	−0.39	0.34	0.08
B_2	−0.04	−0.02	1.00	1.00	−0.38	0.34	0.08
a_1	−0.63	−0.63	−0.39	−0.38	1.00	−0.89	0.76
a_0	0.56	0.56	0.34	0.34	−0.89	1.00	−0.67
N_{10}	−0.74	−0.72	0.08	0.08	0.76	−0.67	1.00

Table 16
Parameter correlation matrix in Example 3 with initial guess for reference values

	A_1	B_1	A_2	B_2	a_1	a_0	N_{10}
A_1	1.00	0.90	0.13	−0.10	−0.58	0.51	−0.72
B_1	0.90	1.00	0.04	−0.02	−0.63	0.56	−0.72
A_2	0.13	0.04	1.00	−0.99	0.36	−0.32	−0.11
B_2	−0.10	−0.02	−0.99	1.00	−0.39	0.34	0.08
a_1	−0.58	−0.63	0.36	−0.39	1.00	−0.89	0.76
a_0	0.51	0.56	−0.32	0.34	−0.89	1.00	−0.67
N_{10}	−0.72	−0.72	−0.11	0.08	0.76	−0.67	1.00

Table 17
Parameter correlation matrix in Example 3 with the reference values optimized with Norm 1

	A_1	B_1	A_2	B_2	a_1	a_0	N_{10}
A_1	1.00	−0.09	0.09	−0.20	0.02	0.00	−0.10
B_1	−0.09	1.00	0.19	−0.02	−0.63	−0.01	−0.72
A_2	0.09	0.19	1.00	−0.04	−0.15	0.00	−0.17
B_2	−0.20	−0.02	−0.04	1.00	−0.38	0.01	0.08
a_1	0.02	−0.63	−0.15	−0.38	1.00	−0.01	0.76
a_0	0.00	−0.01	0.00	0.01	−0.01	1.00	0.00
N_{10}	−0.10	−0.72	−0.17	0.08	0.76	0.00	1.00

Table 18
Parameter correlation matrix in Example 3 with the reference values optimized with Norm 2

	A_1	B_1	A_2	B_2	a_1	a_0	N_{10}
A_1	1.00	−0.07	0.20	−0.20	0.01	0.01	−0.12
B_1	−0.07	1.00	0.14	−0.02	−0.63	−0.01	−0.72
A_2	0.20	0.14	1.00	−0.73	0.16	0.00	−0.18
B_2	−0.20	−0.02	−0.73	1.00	−0.38	0.00	0.09
a_1	0.01	−0.63	0.16	−0.38	1.00	0.00	0.76
a_0	0.01	−0.01	0.00	0.00	0.00	1.00	0.00
N_{10}	−0.12	−0.72	−0.18	0.09	0.76	0.00	1.00

Table 19
Parameter correlation matrix in Example 3 with the reference values optimized with Norm 3

	A_1	B_1	A_2	B_2	a_1	a_0	N_{10}
A_1	1.00	0.55	0.18	−0.18	−0.38	0.00	−0.54
B_1	0.55	1.00	0.19	−0.02	−0.63	−0.01	−0.72
A_2	0.18	0.19	1.00	0.02	−0.18	0.00	−0.17
B_2	−0.18	−0.02	0.02	1.00	−0.39	0.00	0.08
a_1	−0.38	−0.63	−0.18	−0.39	1.00	0.00	0.76
a_0	0.00	−0.01	0.00	0.00	0.00	1.00	0.00
N_{10}	−0.54	−0.72	−0.17	0.08	0.76	0.00	1.00

correlations, but not so small as the ones obtained after minimization of Norms 1 and 2. The obtained results seem to indicate that minimization of the empirical Norm 1 can be very effective for obtainment of low parameter correlations after reparameterization of the model equations.

5. Conclusions

In this work the two-step parameter estimation procedure proposed in a previous work by Schwaab and Pinto (2007) was extended to a more general scenario, where more than one Arrhenius equation is present. Although it is not possible to eliminate all the parameter correlations simultaneously, it was shown through numerical examples that a proper choice of the reference values can reduce the final parameter correlations very significantly. The proposed procedure comprises two steps: in the first step the parameter estimation is performed with an initial guess for the reference values; in the second step some norm of the parameter correlation matrix is minimized through manipulation of reference values.

Three different norms were considered in the present work and the best results were obtained with Norm 1, where the sum of the squares of individual parameter correlations is minimized. Besides, the computation of Norms 2 and 3 involves the calculation of characteristic values and characteristic vectors, leading to more expensive computer calculations. One must observe, though, that the recalculation of the covariance matrix of parameter estimates (and, therefore, of the correlation norm) when the reference temperatures change does not involves any significant increase in the computer costs, since the new covariance matrix can be readily obtained through Eq. (14). Therefore, the larger computer costs of calculating Norms 2 and 3 will only become significant when one is interested in estimating a very large number (tens) of model parameters simultaneously. Consequently, the use of the PSO method for optimization of temperature reference values should be encouraged, due to its inherent capabilities for solving complex problems (with nonconvex behavior and/or multiple minima).

Besides the optimization of the reference temperature value in Arrhenius models, the proposed procedure can also be used for optimum reparameterization of other equations, as shown in Example 3 after definition of a reference rate value for the linear calibration model. With the proposed procedure, the convergence difficulties found during parameter estimation of kinetic models and related to existence of high parameter correlation can be minimized, allowing simultaneously for obtainment of parameters with lower error contents.

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Appendix

Experimental data used in Example 2 (Bates and Watts, 1988)

$C_O \times 10^3$ (mol/L)	$C_X \times 10^4$ (mol/L)	T (K)	r (mol/(mol$_{cat}$ s))	$C_O \times 10^3$ (mol/L)	$C_X \times 10^4$ (mol/L)	T (K)	r (mol/(mol$_{cat}$ s))
5.02	2.00	543.0	116.0	2.49	1.98	563.0	224.0
4.99	1.90	543.0	120.0	5.71	0.49	563.0	198.0
5.04	2.00	543.0	114.0	5.55	3.47	563.0	463.0
5.05	2.00	543.0	117.0	5.49	2.74	563.0	370.0
10.00	3.51	543.0	245.0	5.54	0.95	563.0	258.0
10.10	3.51	543.0	230.0	5.07	1.91	573.0	543.0
10.30	0.50	543.0	106.0	5.02	1.87	573.0	561.0
10.40	3.61	543.0	230.0	5.05	1.92	573.0	560.0
10.10	0.49	543.0	121.0	5.06	1.88	573.0	578.0
10.10	0.50	543.0	115.0	5.00	2.01	573.0	542.0
10.10	0.50	543.0	127.0	1.00	3.50	573.0	197.0
5.70	2.01	563.0	408.0	5.05	2.02	573.0	559.0
5.52	2.01	563.0	380.0	3.06	3.49	573.0	414.0
5.51	2.02	563.0	320.0	5.02	1.98	573.0	467.0
5.51	1.86	563.0	399.0	5.04	2.01	573.0	468.0
5.54	2.02	563.0	371.0	10.17	2.45	573.0	933.0
5.53	1.99	563.0	368.0	4.99	1.87	573.0	509.0
1.08	0.51	563.0	63.0	10.00	2.53	573.0	955.0
7.07	0.99	563.0	333.0	4.96	3.46	573.0	650.0
5.54	1.97	563.0	322.0	10.00	2.53	573.0	902.0
6.05	3.51	563.0	413.0	5.02	1.99	573.0	532.0
5.52	2.02	563.0	344.0	3.99	3.57	573.0	552.0
10.16	1.89	563.0	543.0	1.07	1.96	573.0	184.0
5.52	2.00	563.0	372.0	4.99	3.53	573.0	663.0
6.03	0.49	563.0	229.0	5.03	1.00	573.0	409.0
10.00	2.01	563.0	563.0	2.51	1.99	573.0	326.0
10.10	1.51	563.0	490.0	4.99	2.77	573.0	580.0
8.05	3.54	563.0	595.0	9.06	2.05	573.0	831.0
5.52	1.99	563.0	352.0				

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