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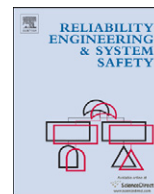
Determination of the uncertainty domain of the Arrhenius parameters needed for the investigation of combustion kinetic models

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ABSTRACT

Many articles have been published on the uncertainty analysis of high temperature gas kinetic systems that are based on detailed reaction mechanisms. In all these articles a temperature independent relative uncertainty of the rate coefficient is assumed, although the chemical kinetics databases suggest temperature dependent uncertainty factors for most of the reactions. The temperature dependence of the rate coefficient is usually parameterized by the Arrhenius equation. An analytical expression is derived that describes the temperature dependence of the uncertainty of the rate coefficient as a function of the elements of the covariance matrix of the Arrhenius parameters. Utilization of the joint uncertainty of the Arrhenius parameters is needed for a correct uncertainty analysis in varying temperature chemical kinetic systems. The covariance matrix of the Arrhenius parameters, the lower and upper bounds for the rate coefficient, and the temperature interval of validity together define a truncated multivariate normal distribution of the transformed Arrhenius parameters. Determination of the covariance matrix and the joint probability density function of the Arrhenius parameters is demonstrated on the examples of two gas-phase elementary reactions.

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1. Introduction

Many models are used in the industry and in environmental protection that include detailed gas-phase reaction mechanisms, consisting of several hundred or even several thousand reaction steps. Here we will concentrate on models that describe high temperature gas kinetic systems. Another series of similar models investigate atmospheric chemistry and the spread of air pollution. The high-temperature chemical kinetic models are used for the analysis and optimization of combustion systems (furnaces, burners and engines) and processes in the chemical industry that include oxidation or pyrolysis. These applications are frequently related to the development of methods for the enhancement of the safety of power stations and chemical plants. Reliability of these predictive models is critical; therefore, many articles have been published about the uncertainty analysis of such models and almost all major methods of uncertainty analysis have been used in this field. The methods applied include local uncertainty analysis [1–7], Monte Carlo analysis with Latin hypercube sampling [4–8], the Morris method [5,6], Sobol sequences [5], the polynomial chaos method [9–13] and the high dimensional model representation (HDMR) [14–17].

The main input information of these uncertainty analysis studies is the uncertainty of the rate parameters. There are chemical kinetics databases that contain information about the uncertainty of rate parameter k. These critical compilations of gas kinetic reactions provide not only the recommended rate parameters, but also report the reliability of the rate coefficients by assigning an uncertainty parameter to them. A temperature range is also given that refers to the range of validity of both the recommended rate coefficient (defined by Arrhenius parameters) and its uncertainty. A series of comprehensive evaluations of high-temperature gas-phase elementary reactions was published by Baulch et al. [18–20]. Similar uncertainty information is available from other combustion chemistry data collections (see e.g. Refs. [21–26]).

In liquid-phase kinetics and atmospheric chemistry, the temperature dependence of a rate coefficient k is described using the Arrhenius expression $k = A\exp(-E/RT)$. In high-temperature gas kinetic systems, the temperature dependence of the rate coefficient is either given by this 'classic' Arrhenius expression, or (in most cases) it is described in the form of the modified Arrhenius expression $k = AT^n \exp(-E/RT)$.

In the combustion reviews of Baulch et al. [18–20], the uncertainty of the rate coefficient is defined by value f in the following way:

$$f = \log_{10}(k^0/k^{\min}) = \log_{10}(k^{\max}/k^0) \tag{1}$$

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where k^0 is the recommended value of the rate coefficient of the reaction, and k^{min} and k^{max} are the possible extreme values; rate coefficients outside the $[k^{min}, k^{max}]$ interval are considered very improbable by the evaluators. In Eq. (1), parameter f and rate coefficients k^0, k^{min} and k^{max} are calculated at a given temperature. Therefore, uncertainty parameter f in general depends on temperature.

Assuming that the minimum and maximum values of the rate coefficients correspond to 3σ deviations [2–7] or 2σ deviations [12,13] from the recommended value on a logarithmic scale, the uncertainty parameter f can be converted [3] at a given temperature T to the standard deviation of the logarithm of the rate coefficient using equation

$$\sigma(\log_{10}k) = \frac{\sigma(\ln k)}{\ln 10} = \frac{1}{m}f(T) \tag{2}$$

where $m=3$ or 2, respectively.

For less than half of the reaction steps in the data evaluation of Baulch et al. [20], they recommend a temperature independent uncertainty factor. For example, for reaction $O+H_2 \rightarrow OH+H$ the uncertainty factor is 0.2 over the range 298–3300 K. For most of the reviewed reaction steps, a temperature dependent uncertainty parameter f is defined, without giving an exact function for the temperature dependence. As an example, for reaction $O+NH_3 \rightarrow OH+NH_2$, rate parameters are recommended in the temperature range of 300–2000 K, and the uncertainty is defined by the following sentence: "± 0.2 at 300 K, rising to ± 0.3 at 2000 K".

In all uncertainty analysis studies cited above [1–17], the uncertainty factor is considered constant in the whole temperature range, even if the uncertainty parameter was taken from the evaluation of Baulch et al. The usual practice is that the highest uncertainty quoted by Baulch et al. in the temperature range is assumed to be valid at all temperatures. Assumption of a temperature independent uncertainty parameter means that only the uncertainty of Arrhenius parameters A is taken into account, while the uncertainties of Arrhenius parameters n and E are considered to be zero. This approach may not cause an error in the investigation of isothermal systems, but it is systematically wrong if the temperature is not constant.

The relation between the uncertainties of rate coefficient k and the Arrhenius parameters has also been discussed in our recent article [27]. In that article the main issue is the self-consistency of the uncertainty parameters as currently provided in the chemical kinetics databases used in the area of combustion and atmospheric chemistry.

In the present article, we show that if the temperature dependence of the rate coefficient is described by an Arrhenius-type equation, then the uncertainty of k has temperature dependence, determined by the uncertainties of the Arrhenius parameters. It is also demonstrated that a good characterization of the uncertainty of the Arrhenius parameters is a starting point of a realistic uncertainty analysis of models using detailed reaction mechanisms in non-isothermal systems.

2. Temperature dependence of the uncertainty of the rate coefficient

The most flexible description of the temperature dependence of rate coefficient k is the modified Arrhenius equation $k(T) = AT^n \exp(-E/RT)$. Taking the logarithm of this equation yields $\ln k(T) = \ln A + n \ln T - E/RT^{-1}$, which can be written in a more compact form using transformed parameters $\kappa(T) := \ln k(T)$, $\alpha := \ln A$, $\varepsilon := E/R$ and column vector notations $\mathbf{p} := (\alpha, n, \varepsilon)^T$ and

$\boldsymbol{\theta} := (1, \ln T, -T^{-1})^T$, where superscript T denotes transposition.

$$\kappa(T) = \alpha + n\ln T - \varepsilon T^{-1} = \boldsymbol{\theta}^T\mathbf{p} = \mathbf{p}^T\boldsymbol{\theta} \tag{3}$$

In this linearized form of the equation, κ is a homogeneous linear function of parameters (α, n, ε). Here κ is considered a temperature dependent random variable, and therefore parameters (α, n, ε), which are determined from κ in a temperature range, are also random variables.

In gas kinetics, the rate coefficient of a given reaction step is usually measured by several research groups over several decades, in different temperature ranges using different experimental techniques. The obtained rate coefficients at many temperatures are used for the determination of a single set of Arrhenius parameters. Within the scope of the Arrhenius expression, parameters α, n and ε are physically well-defined quantities, therefore their joint *pdf* is temperature independent and consequently their expected values $\overline{\mathbf{p}} = (\overline{\alpha}, \overline{n}, \overline{\varepsilon})^T$, standard deviations $\boldsymbol{\sigma_p} = (\sigma_\alpha, \sigma_n, \sigma_\varepsilon)$ and correlations $r_{\alpha n}$, $r_{\alpha\varepsilon}$, $r_{n\varepsilon}$ are also temperature independent. By definition, these have the following properties:

$$0 \leq \sigma_\alpha, \sigma_n, \sigma_\varepsilon \text{ and } -1 \leq r_{\alpha n}, r_{\alpha\varepsilon}, r_{n\varepsilon} \leq 1 \tag{4}$$

The covariance matrix $\boldsymbol{\Sigma_p}$ of parameters (α, n, ε) is defined and can be expanded as [28]

$$\boldsymbol{\Sigma_p} = \overline{(\mathbf{p}-\overline{\mathbf{p}})(\mathbf{p}-\overline{\mathbf{p}})^T} = \begin{bmatrix} \sigma_\alpha^2 & r_{\alpha n}\sigma_\alpha\sigma_n & r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon \\ r_{\alpha n}\sigma_\alpha\sigma_n & \sigma_n^2 & r_{n\varepsilon}\sigma_n\sigma_\varepsilon \\ r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon & r_{n\varepsilon}\sigma_n\sigma_\varepsilon & \sigma_\varepsilon^2 \end{bmatrix} \tag{5}$$

By definition, the covariance matrix is symmetric and positive semi-definite, implying that its determinant is non-negative, which requires that the following be true:

$$0 \leq \sigma_\alpha^2\sigma_n^2\sigma_\varepsilon^2(1 - r_{\alpha n}^2 - r_{\alpha\varepsilon}^2 - r_{n\varepsilon}^2 + 2r_{\alpha n}r_{\alpha\varepsilon}r_{n\varepsilon}) \tag{6}$$

Let us assume that the temperature dependent probability density function of $\kappa(T)$ is known in the temperature range of $[T_1, T_2]$. At a given temperature $T \in [T_1, T_2]$, the expected value and the variance of κ is denoted by $\overline{\kappa}(T)$ and $\sigma_\kappa^2(T)$, respectively. A consequence of Eq. (3) is that there exists a relationship between the expected values of $\kappa(T)$ and (α, n, ε).

$$\overline{\kappa}(T) = \overline{\alpha} + \overline{n}\ln T - \overline{\varepsilon}T^{-1} = \boldsymbol{\theta}^T\overline{\mathbf{p}} = \overline{\mathbf{p}}^T\boldsymbol{\theta} \tag{7}$$

Another consequence of Eq. (3) is the following relationship between the variance of $\kappa(T)$ and the elements of the covariance matrix

$$\sigma_\kappa(T) = \sqrt{\overline{(\kappa(T)-\overline{\kappa}(T))^2}} = \sqrt{\boldsymbol{\theta}^T\boldsymbol{\Sigma_p}\boldsymbol{\theta}} \tag{8}$$

$$\sigma_\kappa(T) = \sqrt{\sigma_\alpha^2 + \sigma_n^2\ln^2 T + \sigma_\varepsilon^2 T^{-2} + 2r_{\alpha n}\sigma_\alpha\sigma_n\ln T - 2r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon T^{-1} - 2r_{n\varepsilon}\sigma_n\sigma_\varepsilon T^{-1}\ln T} \tag{9}$$

According to Eqs. (2) and (9), the variance of $\kappa(T)$ is temperature independent if and only if its uncertainty parameter is temperature independent. Eq. (9) implies that it is possible only if $\sigma_\kappa^2(T) = \sigma_\alpha^2$, and that all other standard deviations and correlations are zero. This trivial solution has been applied previously in all uncertainty studies, when the temperature-independent variance of κ was assumed to be identical to the variance of α, and the variances of the other Arrhenius parameters and their correlations were not considered. However, Arrhenius parameters n and E must also have uncertainty. Eq. (9) shows that if the uncertainties of Arrhenius parameters n and/or E are also considered, then the variance of κ cannot be temperature independent. Eq. (9) suggests that a temperature independent uncertainty is physically unrealistic, and also shows the required functional form of the temperature-dependence of the uncertainty.

The linearized equation for the traditional two-parameter Arrhenius expression is the following:

$$\kappa(T) = \alpha - \varepsilon T^{-1} \tag{10}$$

The corresponding relationship exists between the variance of $\kappa(T)$ and the elements of the covariance matrix:

$$\sigma_\kappa(T) = \sqrt{\sigma_\alpha^2 + \sigma_\varepsilon^2 T^{-2} - 2r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon T^{-1}} \tag{11}$$

Eq. (11) also suggests that a temperature independent uncertainty is physically unrealistic, and it also shows the required functional form of the temperature-dependence of the uncertainty.

3. Determination of the covariance matrix of the Arrhenius parameters

Equations deduced for the temperature dependence of $\sigma_\kappa(T)$ (see Eqs. (9) and (11)) together with the uncertainty information given in the chemical kinetics databases (see Eq. (2)) can be used for the determination of the covariance matrix of the Arrhenius parameters.

In the case of a three-parameter modified Arrhenius expression, based on Eq. (9), the elements of the covariance matrix can be determined by a least squares fit to the uncertainty data using the following function:

$$f(T) = M\sqrt{\sigma_\alpha^2 + \sigma_n^2 \ln^2 T + \sigma_\varepsilon^2 T^{-2} + 2r_{\alpha n}\sigma_\alpha\sigma_n \ln T - 2r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon T^{-1} - 2r_{n\varepsilon}\sigma_n\sigma_\varepsilon T^{-1}\ln T} \tag{12}$$

where $M = 3/\ln 10$ or $2/\ln 10$, depending on the assumption if $k^{\min}$ and $k^{\max}$ correspond to 3σ or 2σ limits, respectively.

When determining the parameters, the linear (Eq. (4)) and multivariate non-linear (Eq. (6)) inequality constraints for the standard deviations and correlations also have to be taken into account. Only a few data fitting software are capable of handling non-linear constraints and one of them is EASY-FIT Express [29]. In this case the uncertainty of the rate coefficient has to be known at least at 6 different temperatures to determine the 6 independent elements of the covariance matrix of the three Arrhenius parameters.

For the two-parameter (α, ε) expression, the function to be used in fitting is

$$f(T) = M\sqrt{\sigma_\alpha^2 + \sigma_\varepsilon^2 T^{-2} - 2r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon T^{-1}} \tag{13}$$

In this case, only constraints defined in Eq. (4) have to be taken into account and the uncertainty has to be known at least at 3 temperatures. Note, that Hébrard et al. [30] recommended an expression similar to Eqs. (13) for the traditional Arrhenius equation to characterize the temperature dependence of the uncertainty of the rate coefficients.

Even if the number of uncertainty points is equal to that minimally required, the above equations with optimized parameters may not reproduce these points exactly, since Eqs. (12) and (13) are not fully flexible. If the uncertainties are provided at more temperatures than minimally required, then we have an over-determined set of parameters. In both cases, the optimal

values can be determined by a least squares fit, taking into account the constraints defined in Eqs. (4) and (6).

4. The joint normal *pdf* of the Arrhenius parameters

Till this point, no particular type of probability density function (*pdf*) was assumed for either the rate coefficient or the Arrhenius parameters. Some methods of uncertainty analysis [31] calculate the variance of the simulation results from the variances (or the covariance matrix) of the parameters. For these types of methods the covariance matrix of the Arrhenius parameters provides enough information. Other methods of uncertainty analysis are able to calculate the probability density function (*pdf*) of the simulation results using the joint *pdf* of the parameters. Therefore, it is advantageous to define an approximate joint probability density function of the Arrhenius parameters.

There is no consensus in the literature on the form of the probability density function (*pdf*) of $\ln k$. In the data evaluations, no assumed distribution of the rate coefficient is stated. In some publications, uniform distribution is assumed between the $k^{\min}$ and $k^{\max}$ values. According to another approach, the recommended $\ln k^0$ has high probability and the extreme values $\ln k^{\min}$ and $\ln k^{\max}$ have very low probability. Therefore, it is assumed in several publications [4,5,7], that the *pdf* can be approximated by a normal distribution at any temperature, truncated at the $\ln k^{\min}(T)$ and $\ln k^{\max}(T)$ values.

$$\rho_1(\kappa; T) = \frac{1}{\sqrt{2\pi}\,\sigma_\kappa(T)}\exp\left[-\frac{(\kappa(T) - \overline{\kappa(T)})^2}{2\sigma_\kappa^2(T)}\right] \tag{14}$$

where $\ln k^{\min}(T) \leq \kappa(T) \leq \ln k^{\max}(T)$.

As a matter of fact, considering a truncated normal distribution for $\ln k$ is just an assumption.

In a recent article [27], a detailed mathematical proof is given for the statements below. Here only a brief summary is provided about the relationship between the temperature dependent probability density function (*pdf*) of the rate coefficients and the temperature independent *pdf* of the Arrhenius parameters.

The joint *pdf* of the Arrhenius parameters uniquely determines the *pdf* of the rate coefficient at every temperature. If the temperature dependence of the rate coefficient is described by a 3-parameter (2-parameter) Arrhenius equation, then the $\ln k$ values are uncorrelated only up to 3 (2) temperatures. The random $\ln k$ values at all other temperatures are correlated. If the $\ln k$ values are sampled independently from each other at several (more than 3 (or 2)) temperatures, then the set of these random $\ln k$ values is physically unrealistic. Using such data leads to misleading uncertainty analysis results. A joint multivariate normal distribution of Arrhenius parameters (α, n, ε) implies a normal distribution for $\ln k$ at any temperature.

The joint probability density function of a uni- or multivariate normal distribution of parameter vector **p** of dimension N is defined in Eq. (15). It is completely determined by the vector $\overline{\mathbf{p}}$ of expectation values and the covariance matrix $\Sigma_{\mathbf{p}}$.

$$\rho_N(\mathbf{p}; \overline{\mathbf{p}}, \Sigma_{\mathbf{p}}) = \frac{\exp[-1/2(\mathbf{p}-\overline{\mathbf{p}})^{\mathrm{T}}\Sigma_{\mathbf{p}}^{-1}(\mathbf{p}-\overline{\mathbf{p}})]}{(2\pi)^{N/2}\sqrt{\det\Sigma_{\mathbf{p}}}} \tag{15}$$

In the case of multivariate normal distribution, zero correlation between two parameters means independence.

Table 1
Data of the reactions used in the examples. Parameter A is given in units mole, cm and s.

#	Reaction	α	n	ε (K)	Temperature interval (K)	Uncertainty f
R1	$C_6H_6 + OH \rightarrow C_6H_5 + H_2O$	30.456	–	2302	298–1500	298 K:0.3 500–1500 K:0.1
R2	$CH_4 + O \rightarrow CH_3 + OH$	12.99	2.5	3310	400–2500	400 K:0.5 600–2500 K:0.3

5. Examples

The covariance matrices of the Arrhenius parameters of two reactions were determined using the equations derived in the previous sections. The examples were chosen from the latest evaluation of Baulch et al. [20]. The Arrhenius parameters, the temperature range of validity, and the uncertainty information for sample reactions are given in Table 1. The uncertainty parameters were converted to variances by assuming 3σ truncation limit. The determined corresponding standard deviations and correlations are given in Table 2.

Temperature dependence of the rate coefficient of reaction $C_6H_6 + OH \rightarrow C_6H_5 + H_2O$ (R1) is defined by a two-parameter (α, ε) original Arrhenius equation in temperature interval 298–1500 K. The uncertainty value is $f = 0.3$ at temperature 298 K and it is considered constant $f = 0.1$ in the temperature range 500–1500 K. Using Eq. (13), the elements of the covariance matrix were fitted to the following uncertainty points: 0.3 at $T = 298$ K and 0.1 at temperatures 500, 700, 900, 1100, 1300 and 1500 K. The optimized parameters of the covariance matrix are given in Table 2 (row R1). The transformed Arrhenius parameters are highly correlated; the correlation coefficient is $r_{\alpha\varepsilon} = 0.893$. The obtained $f(T)$ function well follows the uncertainty points as the solid line shows in Fig. 1.

Fig. 2 presents the temperature dependent *pdf* of transformed rate coefficient κ. The variance of κ is smaller and therefore the *pdf* is narrower at intermediate temperatures. Because at each temperature the area under the *pdf* is equal to one, therefore the peak value of the *pdf* is higher at intermediate temperatures. Fig. 3 shows a 3D plot of the joint *pdf* of the Arrhenius parameters. It is a typical two-dimensional normal distribution for highly correlated parameters.

The rate coefficient of reaction $CH_4 + O \rightarrow CH_3 + OH$ (R2) changes with temperature according to the modified Arrhenius equation. Uncertainty $f = 0.5$ was defined [20] at 400 K and the

Fig. 2. 3D graph of the temperature dependent *pdf* of variable $\kappa = \ln k$ for reaction R1.

Fig. 3. 3D graph of the joint *pdf* of the Arrhenius parameters for reaction R1.

uncertainty was considered constant $f = 0.3$ in the temperature interval of 600–2500 K. The definition of the covariance matrix of the Arrhenius parameters, according to Eq. (12) requires the knowledge of the uncertainty value at least at 6 different temperatures. In our calculations, the following uncertainties were considered: $f = 0.5$ at 400 K and $f = 0.3$ at temperatures 600, 1000, 1500, 2000 and 2500 K. These points are indicated by circles in Fig. 4. The optimized parameters of the covariance matrix are given in Table 2 (row R2). There are very strong correlations among the three transformed Arrhenius parameters; the correlation coefficients are very close to ± 1. As Fig. 4 shows, the obtained $f(T)$ function (solid line) very well follows the uncertainty points.

6. Conclusions

At the simulation of constant temperature kinetic systems, the rate coefficients are the parameters used in the model. During the

Table 2
Determined elements of the covariance matrix of the Arrhenius parameters for the reactions defined in Table 1.

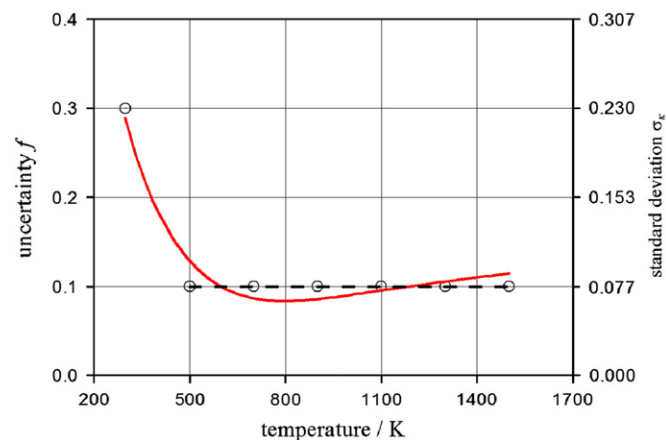| Reaction	σ_α	σ_n	σ_ε (K)	$r_{\alpha n}$	$r_{\alpha\varepsilon}$	$r_{n\varepsilon}$
R1	0.1427	–	101.3	–	0.89296	–
R2	3.463	0.4205	501.9	−0.99779	0.99859	−0.99991

Fig. 1. Uncertainty of reaction R1 is $f = 0.3$ at temperature 298 K and it is considered constant $f = 0.1$ in the temperature range 500–1500 K. Function $f(T)$ was fitted to the values indicated by circles; the fitted function is plotted by a solid line. The corresponding elements of the covariance matrix are given in rows R1 of Table 2.
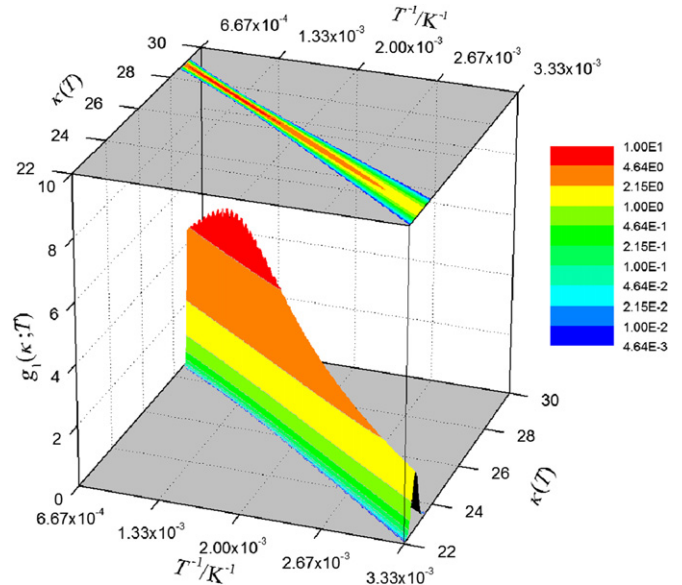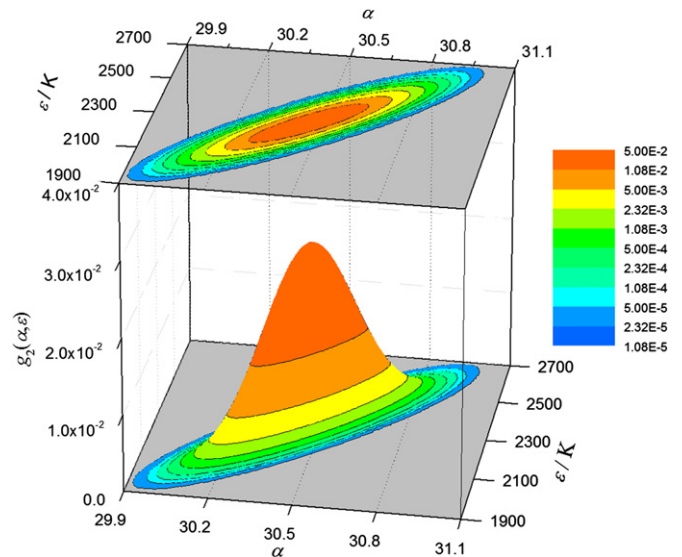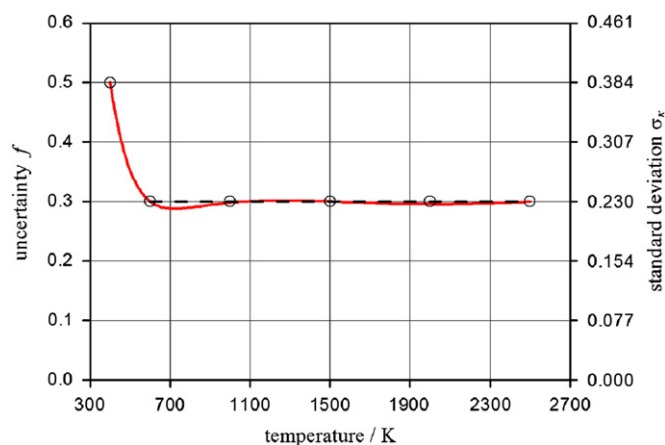
Fig. 4. Uncertainty of reaction R2 is $f = 0.5$ at temperature 400 K and it is considered constant $f = 0.3$ in the temperature range 600–2500 K. Function $f(T)$ was fitted to the values indicated by circles; the fitted function is plotted by a solid line. The corresponding elements of the covariance matrix are given in rows R2 of Table 2.

uncertainty analysis, the values of these parameters are changed according to the uncertainty information obtained from the chemical kinetics databases. When varying temperature kinetic systems are simulated, the values of rate coefficients belonging to the actual temperature are calculated in each step from the Arrhenius parameters. Therefore, the effect of the change in Arrhenius parameters should be investigated during the uncertainty analysis. However, in all published uncertainty studies of combustion models based on detailed reaction mechanisms, a constant relative uncertainty of the rate coefficient was assumed as input information on the uncertainty of parameters. This approach may have a practical reason: the chemical kinetics databases do not contain the uncertainty of the Arrhenius parameters. In these uncertainty studies, the largest uncertainty value suggested in the database within the temperature interval was usually selected as the temperature independent uncertainty parameter. Assuming a temperature independent uncertainty factor means that the uncertainty of rate coefficient k was considered to be equal to the uncertainty of Arrhenius parameter A, while the uncertainties of Arrhenius parameters n and E were considered zero. This is a physically unrealistic assumption and the uncertainty information used in these studies did not correspond to the uncertainty information present in the chemical kinetics databases.

In this article we suggest another approach. Based on the uncertainty information present in the chemical kinetics databases, uncertainty parameter values should be selected at several temperatures. Using Eq. (12) for the modified (3-parameter) Arrhenius expression or Eq. (13) for the original (2-parameter) Arrhenius expression (by taking into account also constraints (4) and (6)), the elements of the covariance matrix of the Arrhenius parameters can be fitted to the selected uncertainty values.

Certain methods of uncertainty analysis require the covariance matrix of the parameters only as input. However, several other methods (including the Monte Carlo analysis) need the joint probability density function (pdf) of the parameters. We have shown that if the transformed Arrhenius parameters ($\alpha = \ln A, n, \varepsilon = E/R$) have multivariate normal distribution, then $\ln k$ has normal distribution at any temperature. Also, the main values and the covariance matrix of the Arrhenius parameters, the bounds for the rate coefficient (defined e.g. by thresholds $\pm 2\sigma$ or $\pm 3\sigma$) and the temperature interval of validity *together* define a truncated multivariate normal distribution for the joint pdf of the

transformed Arrhenius parameters. The resulting pdf of the rate coefficients will be a truncated normal distribution at any temperature. The generated joint pdf of the Arrhenius parameters can be used for Monte Carlo uncertainty studies.

A computer code is available for the determination of the covariance matrix of the Arrhenius parameters from the uncertainty parameter of the rate coefficient in web page http://garfield.chem.elte.hu/Combustion/Arrhenius.htm.

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