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Numerical investigation of the uncertainty of Arrhenius parameters

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Abstract The temperature dependence of rate coefficient k is usually described by the Arrhenius expression $\ln k = \ln A - (E/R)T^{-1}$. Chemical kinetics databases contain the recommended values of Arrhenius parameters A and E, the uncertainty parameter $f(T)$ of the rate coefficient and temperature range of validity of this information. Taking $\ln k$ as a random variable with known normal distribution at two temperatures, the corresponding uncertainty of $\ln k$ at other temperatures was calculated. An algorithm is provided for the generation of the histogram of the transformed Arrhenius parameters $\ln A$ and E/R, which is in accordance with their 2D normal probability density function (*pdf*). The upper and the lower edges of the 1D normal distribution of $\ln k$ correspond to the two opposite edge regions of the 2D *pdf* of the transformed Arrhenius parameters. Changing the temperature, these edge regions move around the 2D cone. The rate parameters and uncertainty data belonging to reactions $H + H_2O_2 = HO_2 + H_2$ and $O + HO_2 = OH + O_2$ were used as examples.

Keywords Chemical kinetics · Arrhenius equation · Rate coefficient ·
Uncertainty parameter · Probability density function

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1 Introduction

The temperature dependence of rate coefficient k is usually described by the Arrhenius equation $k(T) = A \exp(-E/RT)$, where T is the temperature in Kelvin, R is the gas constant and temperature independent parameters A and E are called the preexponential factor and the activation energy, respectively. The Arrhenius equation is frequently used in the following transformed form:

$$\ln k = \ln A - \frac{E}{R}T^{-1} \tag{1}$$

According to Eq. (1), $\ln k$ is a linear function of T^{-1} and the $\ln k$ *versus* T^{-1} representation is called the Arrhenius plot. The traditional Arrhenius equation (1) is used in liquid phase kinetics and in atmospheric chemistry. In combustion kinetics further expressions, not be discussed here, are also used [1] to describe the temperature dependence of the rate coefficient.

The chemical kinetic databases for each elementary reaction provide the chemical equation, the Arrhenius parameters, and the temperature range, in which the recommendation is valid. In the kinetics of gas phase reactions, application of an uncertainty parameter is common that characterizes the uncertainty of rate coefficient k in this temperature interval. In general, the uncertainty parameter $f(T)$ is a function of temperature. Uncertainty parameter f_j of reaction j is usually defined [2] in the following way:

$$f_j(T) = \log_{10}\left(\frac{k_j^0(T)}{k_j^{\min}(T)}\right) = \log_{10}\left(\frac{k_j^{\max}(T)}{k_j^0(T)}\right), \tag{2}$$

where k_j^0 is the recommended value of the rate coefficient calculated from the listed Arrhenius parameters A_j^0 and E_j^0 using equation $k_j^0(T) = A_j^0 \exp\left(-E_j^0/RT\right)$, while $k_j^{\min}(T)$ and $k_j^{\max}(T)$ are the possible extreme values of k_j at temperature T. Rate coefficients outside the $[k_j^{\min}(T), k_j^{\max}(T)]$ interval are considered to be highly improbable. It is usually assumed that the minimum and maximum values of the rate coefficients correspond to 3σ deviations [3–8] or 2σ deviations [9,10] from the recommended values on a logarithmic scale, thus uncertainty f can be converted [4] at a given temperature T to the variance of $\ln k$ using equation

$$\sigma^2\left(\ln\left(k_j(T)\right)\right) = \left(\frac{f_j(T)\ln 10}{n}\right)^2, \tag{3}$$

where $n = 3$ or 2, respectively. Usually normal distribution is assumed [3–10] for parameter $\ln k$, truncated at the $k^{\min}$ and $k^{\max}$ values.

When the Arrhenius parameters are determined from chemical kinetics measurements, the experimental data allow the determination of the uncertainty of these parameters. This topic has been discussed in the classic articles of Cvetanović et al. [11–13].

A numerical study of the uncertainties of Arrhenius parameters has been carried out by Héberger et al. [14]. They stated that the Arrhenius parameters calculated from rate coefficients are highly correlated and this correlation should be characterized by a correlation matrix. Estimation of Arrhenius parameters A and E using the logarithmic form (1) of the Arrhenius equation was investigated by Klička and Kubáček [15], and by Sundberg [16], based on different assumptions for the errors of the measured rate coefficients. Rodríguez-Aragón and López-Fidalgo [17] discussed the determination of the Arrhenius parameters from the point of view of experimental design theory. Schwaab and his coworkers [18,19] studied the question of the selection of the optimum reference temperature to decrease the correlation between the parameters of the reparameterized Arrhenius equation. Najm et al. [20] calculated the Arrhenius parameters of a single-step global reaction for the ignition of methane from simulated methane concentration—time data with added Gaussian noise. They found that the joint probability density function (*pdf*) of the transformed Arrhenius parameters $\ln A$ and $\ln E$ was almost of a 2D normal distribution.

In all articles listed in the previous paragraph, the uncertainty of the Arrhenius parameters was calculated from real or simulated experimental data. An entirely different approach is the investigation of the relation between the uncertainty of rate coefficient k and the uncertainty of the Arrhenius parameters. Nagy and Turányi recently published an article [1] in which an equation is derived that relates the temperature dependent variance of $\ln k$ and the covariance matrix of the Arrhenius parameters. They stated that if the Arrhenius parameters of Eq. (1) have temperature independent 2D joint normal distribution, then $\ln k$ has temperature dependent 1D normal distribution at each temperature, and random variables $\ln k(T)$ are uncorrelated at not more than two temperatures. If $\ln k(T)$ is a random variable having such a feature, then the corresponding 2D normal distribution of the Arrhenius parameters can be unambiguously determined.

The present article is a kind of continuation of the paper of Nagy and Turányi [1]. Random $\ln k$ values were generated at two temperatures, and using Arrhenius equation (1), the corresponding random $\ln k$ values were calculated at other temperatures. An algorithm is presented to calculate the histogram of the Arrhenius parameters starting from the uncertainty information for $\ln k$. The features of the histograms of these random variables were analyzed. In all calculations, rate parameters and uncertainty data taken from the latest review of Baulch et al. [2] were used. The data for the two investigated reactions are listed in Table 1.

Table 1 Data of reactions used as examples

	A_0	$\ln(A_0)$	E_0/R	T_1	T_2	Uncertainty parameter
Unit	$s^{-1}cm^3mole^{-1}$	–	K	K	K	–
R1 $H + H_2O_2 = HO_2 + H_2$	1.69×10^{12}	28.16	+1,890	280	1,000	$f = 0.5(T = 280 - 1,000\,K)$
R2 $O + HO_2 = OH + O_2$	1.63×10^{13}	30.42	−224	220	1,000	$f = 0.1$ at 220 K rising to $f = 0.5$ at 1,000 K

The Arrhenius parameters and the uncertainty data are assumed to be valid in temperature range $[T_1, T_2]$

2 Case 1: equal uncertainty of the rate coefficient is defined at two temperatures

The two parameters of the Arrhenius equation is determined if the values of the rate coefficient are known at two different temperatures. Consequently, if these rate coefficients are independent random variables, then the Arrhenius parameters will be random parameters and the rate coefficient values calculated at other temperatures will not be independent random variables. This situation is investigated in this section.

The following algorithm considers the uncertainty of the rate coefficient k at two temperatures. The variance of the rate coefficient was calculated from the uncertainty parameter f using Eq. (3) with parameter $n = 3$, and normal distribution was assumed, which was truncated at $\pm 3\sigma$.

1. Generation of m pairs of random points $\ln k(T_1)$ and $\ln k(T_2)$ independently from each other having uncertainty $f(T_1)$ and $f(T_2)$ at temperatures T_1 and T_2, respectively.
2. The Arrhenius parameters were calculated using Eq. (1) for each pair of $\ln k$ points.
3. At a selected T, m values of $\ln k(T)$ are calculated from the $(\ln A, E/R)$ pairs obtained in the previous step.

For many reactions, the chemical kinetic databases define a temperature independent uncertainty parameter. For example, the uncertainty of the rate coefficient of reaction R1 (H + H$_2$O$_2$ = HO$_2$ + H$_2$) is considered constant $f = 0.5$ by Baulch et al. [2] in the temperature interval of evaluation. (see Table 1). In our calculations, $m = 10^8$ pairs of rate coefficients were generated at temperatures 280 K and 1,000 K independently of each other and the corresponding transformed Arrhenius parameters were determined. The question is if the $\ln k$ values calculated at mid temperatures in step 3 also have a normal distribution and what is the variance that belongs to ln k at this temperature?

Figure 1 shows the histogram of the $\ln k$ values calculated at $T = 450$ K. The histogram clearly corresponds to a normal distribution. It has been expected since a linear combination of two random variables having normal distribution is also of normal distribution [21] and the $\ln k(450\,\text{K})$ values were obtained via multiplications and additions from the $\ln k(280\,\text{K})$ and the $\ln k(1,000\,\text{K})$ values using Eq. (1).

The calculated empirical standard deviation of $\ln k$ at 450 K was $\sigma(\ln k) = 0.275$. The corresponding uncertainty parameter, obtained from Eq. (3), is $f = 0.3587$, which is less than the $f = 0.50$ value used at the extreme temperatures. In a similar way, uncertainty f was calculated for the whole temperature interval and Fig. 2 shows f as a function of temperature. As expected, f is equal to 0.50 at $T_1 = 280$ K and at $T_2 = 1,000$ K, but it is always lower at mid-temperatures. The lowest value is $f = 0.355$ at temperature $T = 440$ K. This result is in accordance with the alignment of the random $\ln k(T)$ lines on an Arrhenius plot, when both $\ln A$ and E/R has uncertainty. Figure 3 that shows ten randomly selected $\ln k$ functions belonging to ten different $(\ln A, E/R)$ pairs, using an Arrhenius plot. Many lines cross each other, therefore the variance of $\ln k$ should be smaller at mid-temperatures.
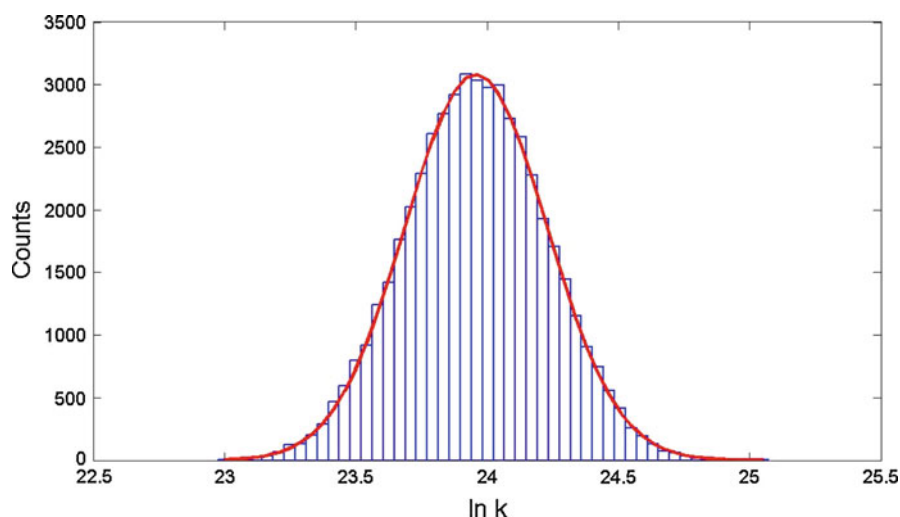
Fig. 1 The histogram of the ln k values calculated at $T = 450$ K for reaction R1. The line is the fitted Gaussian function
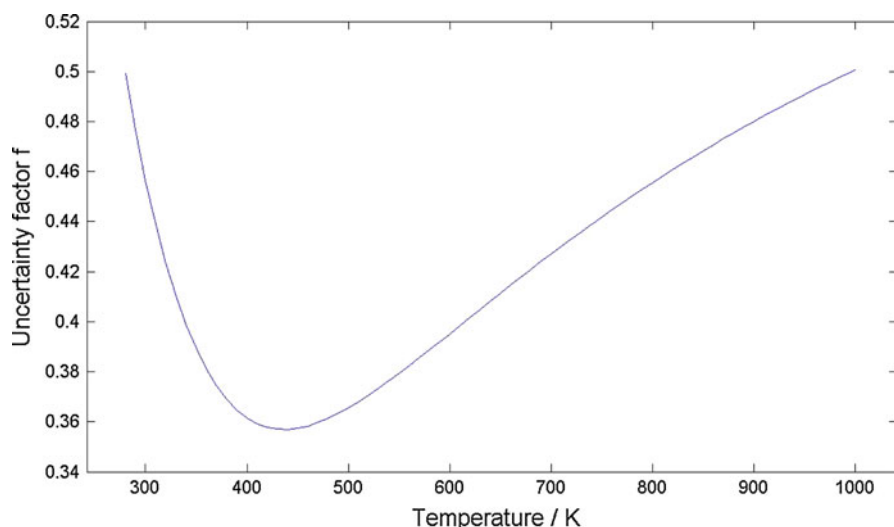

Fig. 2 Temperature dependence of uncertainty parameter f, calculated from the random pairs of Arrhenius coefficients for reaction R1 (Case 1)

The conclusion is that if at temperatures T_1 and T_2 the rate parameters have identical uncertainty and are sampled independently, then the uncertainty of ln k, calculated from the uncertainty of the Arrhenius parameters, is smaller at middle temperatures.

An alternative approach is to change ln k at both extreme temperatures using the same random multiplication factor. The values of this factor are selected in such a way to reproduce the assumed ln k distribution at both temperatures. As Fig. 4 shows, the corresponding ln k lines are parallel, indicating that all random pairs of rate
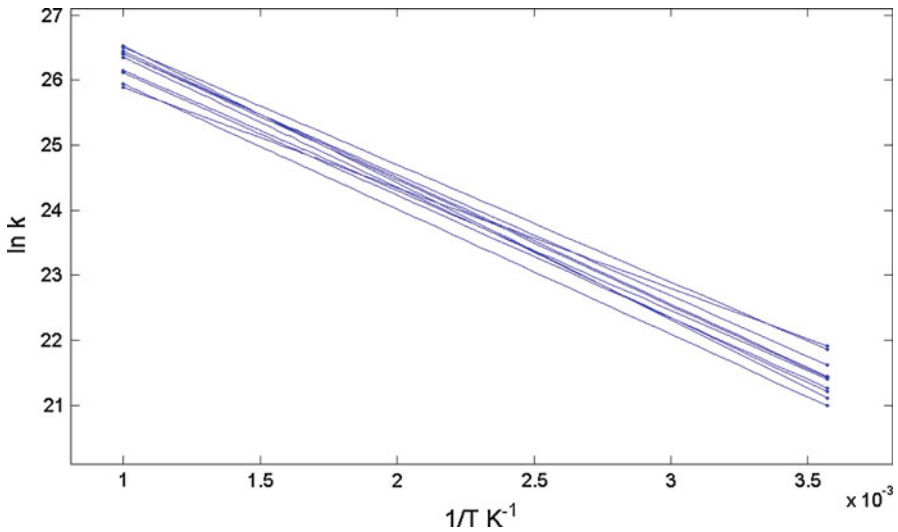
Fig. 3 Arrhenius plot of the rate coefficient—temperature functions, obtained from $n = 10$ random ($\ln A$, E/R) pairs (Case 1)
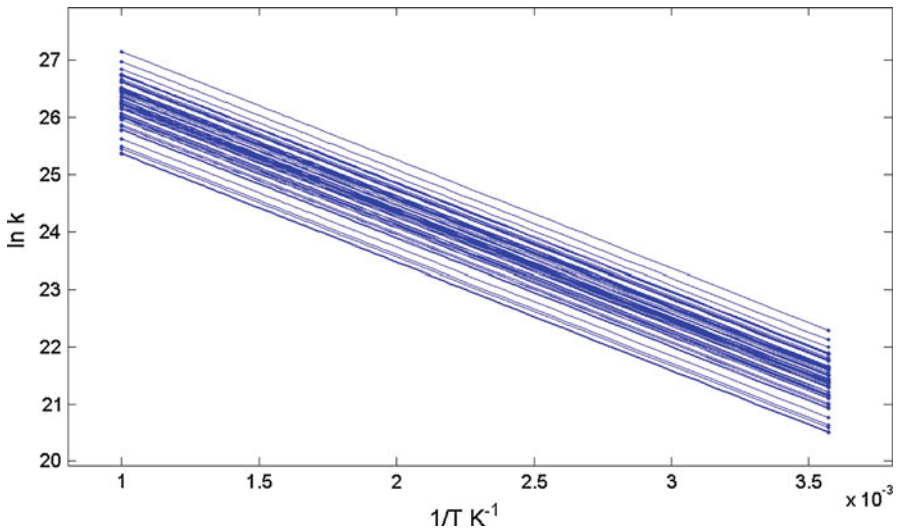
Fig. 4 Arrhenius plot of the rate coefficient—temperature functions, obtained from fully correlated $\ln(k_1)$ and $\ln(k_2)$ values of reaction R1

coefficients result in identical E/R, but different $\ln A$. Thus, the variance of $\ln k$ is identical in the whole temperature range, it is equal to the variance of $\ln A$, and the value of E/R does not have uncertainty. This is a physically not realistic scenario, since the activation energy of reactions cannot be known without uncertainty.

Several conclusions can be obtained from the calculations presented in this section. If the random $\ln k$ values are sampled independently, this determines the distribution

of the Arrhenius parameters and also the uncertainty of $\ln k$ at other temperatures. Knowing the probability density function of $\ln k$ at two different temperatures is not enough for the characterization of the uncertainty of the Arrhenius parameters; the correlation of random variables $\ln k(T_1)$ and $\ln k(T_2)$ also has to be known. A temperature independent uncertainty parameter of $\ln k$ is possible only if the activation energy is known with full certainty, which is physically not possible. These conclusions are in accordance with the results of Nagy and Turányi [1] obtained in a different way.

## 3 Case 2: uncertainty of the rate coefficient is monotonically changing with temparature

One of the results of the calculations presented in the previous section is that the geometry of the Arrhenius plot implies that if the random $\ln k$ values are independent at the extreme temperatures, then the $f(T)$ function will have a minimum at a mid temperature. The following algorithm is suggested that produces monotonically increasing or decreasing $f(T)$ function between two selected temperatures. According to the review of Baulch et al. [2], this type of uncertainty—temperature function is characteristic for many reactions. Usually the room temperature measurements have low uncertainty, while at higher temperatures the experimental methodology is more difficult and therefore $f_1 < f_2$ if $T_1 < T_2$. In the opposite case the algorithm below is still applicable by reversing the role of T_1 and T_2.

Assume that recommended Arrhenius parameters A^0 and E^0 are available from a database in temperature interval $[T_1, T_2]$ and uncertainty parameters f_1 and $f_2(f_1 < f_2)$ are known at temperatures T_1 and T_2, respectively. The algorithm consists of the following steps:

1. Selection of temperature T_0 and a corresponding uncertainty $f_0(T_0 \leq T_1$ and $f_0 < f_1)$. Generation of m pairs of random rate coefficient points $\ln k(T_0)$ and $\ln k(T_2)$ that belong to temperatures T_0 and T_2 by assuming independent normal distribution for $\ln k$ (truncated at $\pm 3\sigma$), using variance σ belonging to uncertainty parameters f_0 and f_2, respectively.
2. Calculation of Arrhenius parameters $\ln A$ and E/R from each pair of $(\ln k(T_0)$, $\ln k(T_2))$ points. The obtained m pairs of $(\ln A, E/R)$ values are used for a statistical characterization of the $(\ln A, E/R)$ distribution.
3. Optimization of temperature T_0 to achieve that $f(T_1)$ calculated from the $(\ln A, E/R)$ values at T_1 becomes equal to f_1 and $f(T)$ is a continuously increasing function in temperature interval $[T_1, T_2]$.

This algorithm results in m points of $(\ln A, E/R)$ pairs in such a way that the histogram of $\ln k$ at temperatures T_1 and T_2 correspond to uncertainty parameters f_1 and f_2, respectively.

This method is illustrated on the example of reaction R2 : $O + HO_2 = OH + O_2$. The uncertainty of the rate coefficient of this reaction is characterized by Baulch et al. [2] with the following words: "$f = 0.1$ at $220 K$ rising to $f = 0.5$ at $1,000 K$" (see Table 1). Using the algorithm above, $f_2 = 0.5$ was used at $T_2 = 1,000 \, K$, and $f_0 = 0.08$ was selected. By means of a search code for minimizing the difference between $f(T_1)$ and f_1, T_0 was changed from $220 \, K$ till $200.0 \, K$ when the calculated
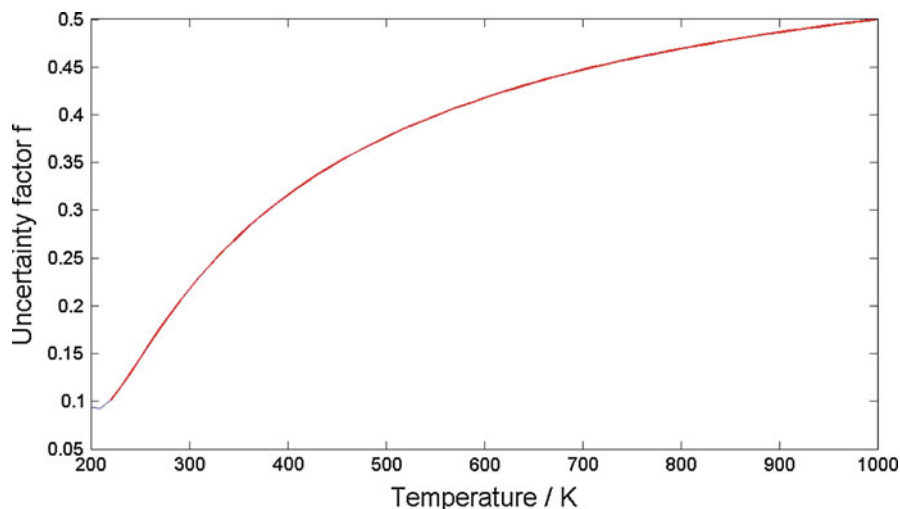
Fig. 5 Temperature dependence of uncertainty parameter f, calculated from the random pairs of Arrhenius coefficients for reaction R2 using the recommended algorithm

$f(T_1)$ became almost equal to $f_1 = 0.1$. In each iteration step $m = 10^5$ was used, while in the final calculation $m = 10^8$ random (ln $A, E/R$) pairs were computed. Figure 5 shows that the obtained $f(T)$ curve is monotonically increasing and passes through points $f(220 \text{ K}) = 0.1$ and $f(1,000 \text{ K}) = 0.5$.

4 The histogram and the joint *pdf* of the Arrhenius parameters

Since increasing uncertainties are assumed for many reactions, the histogram of the Arrhenius parameters obtained for reaction R2 : O + HO$_2$ = OH + O$_2$ will be investigated further. Nagy and Turányi [1] predicted that the corresponding *pdf* of the transformed Arrhenius parameters must have a 2D normal distribution.

The distribution of the obtained transformed Arrhenius parameters ln A and E/R can be visualized by a histogram. A 100×100 grid was defined between limits min(ln A) − max(ln A) and min(E/R) − max(E/R). The number of (ln $A, E/R$) pairs belonging to each rectangle defined by this grid was counted and this number was attributed to the middle coordinate of the rectangle. Figure 6 shows the 2D histogram. The peak of the histogram is at ln $A = 30.69$, $E/R = −205$ K, which is close to the nominal value of ln $A = 30.42$, $E/R = −224$ K. It is clear that the (ln $A, E/R$) values are correlated, that is a small change of ln A can be compensated with an appropriate adjustment of E/R to reproduce a similar $k(T)$ value in a wide range of temperature.

The histogram of the transformed Arrhenius parameters ln A and E/R was used to determine the parameters of the *pdf* of the transformed Arrhenius parameters. Each number in the grid was divided by m, the total number of points, and the obtained values were approximated using the following general equation [21] for a 2D normal distribution:
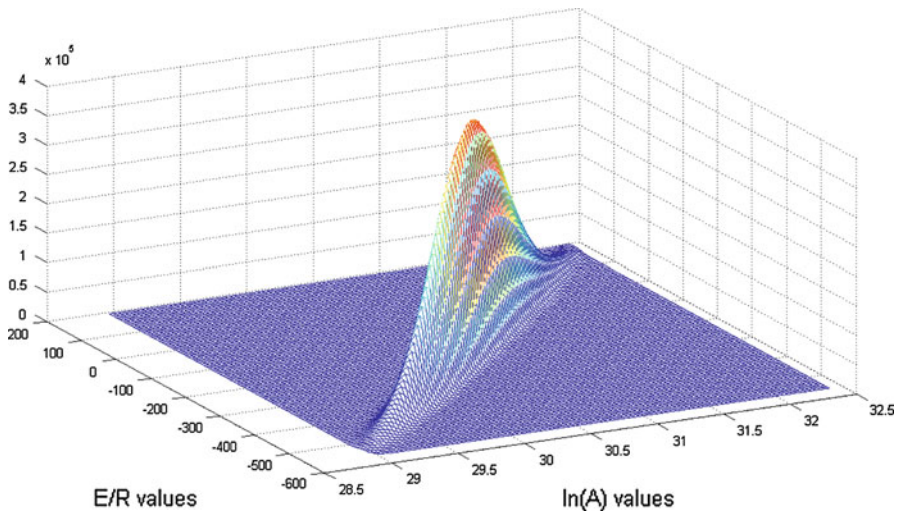
**Fig. 6** 2D histogram of the $(\ln A, E/R)$ pairs of Arrhenius parameters, corresponding to reaction R2

$$g_2(x_1, x_2) = \frac{\exp\left[-\frac{1}{2(1-r_{12}^2)}\left(\frac{(x_1-\bar{x}_1)^2}{\sigma_1^2} + \frac{(x_2-\bar{x}_2)^2}{\sigma_2^2} - \frac{2r_{12}(x_1-\bar{x}_1)(x_2-\bar{x}_2)}{\sigma_1\sigma_2}\right)\right]}{2\pi\sigma_1\sigma_2\sqrt{1-r_{12}^2}} \tag{4}$$

The fitted parameters are the following: $\sigma_{lnA} = 0.4959$, $\sigma_{E/R} = 112.38\,\text{K}$, $r = 0.9876$. The maximum of the fitted function is $\ln A = 30.49$ and $E/R = -221.76$, which is in good accordance with the location of the largest value in the grid. Correlation coefficient r is close to one, showing a very strong correlation between the transformed Arrhenius parameters. The error of approximation was very low (the highest deviation is 1.65 % and the average of absolute deviations is 0.52 %), indicating that the histogram really corresponds to a 2D normal distribution.

The $f(T)$ obtained by this algorithm is not unique, since *e.g.* other f_0 and optimized T_0 values may also result in a curve that passes through the $f_1(T_1)$ and $f_2(T_2)$ points. This means that the *pdf* generated in this way is also not unique. However, we may claim that the obtained *pdf* of the Arrhenius parameters corresponds to the uncertainty definition given in the kinetic database.

Using the most probable $\ln A$ and E/R values (the peak of the cone) in Eq. (1), the most probable $\ln k$ value is obtained, belonging to peak of the $\ln k$ bell curve (*c. f.* Fig. 1). It is also expected that the less probable $\ln k$ values (belonging to the lower or upper edges of the bell curve) correspond to edge regions of the $\ln A - E/R$ cone, but the actual locations of the corresponding regions depend on temperature.

In Fig. 7a–f, 1,000 randomly selected $(\ln A, E/R)$ points of reaction R2 are plotted. These points well outline the 2D normal distribution. Among these points, triangles indicate those points that belong to the low $\ln k$ values having less than 2% probability, while the squares indicate those that belong to the high $\ln k$ values having less than 2% probability at a given temperature. The triangles and the squares are
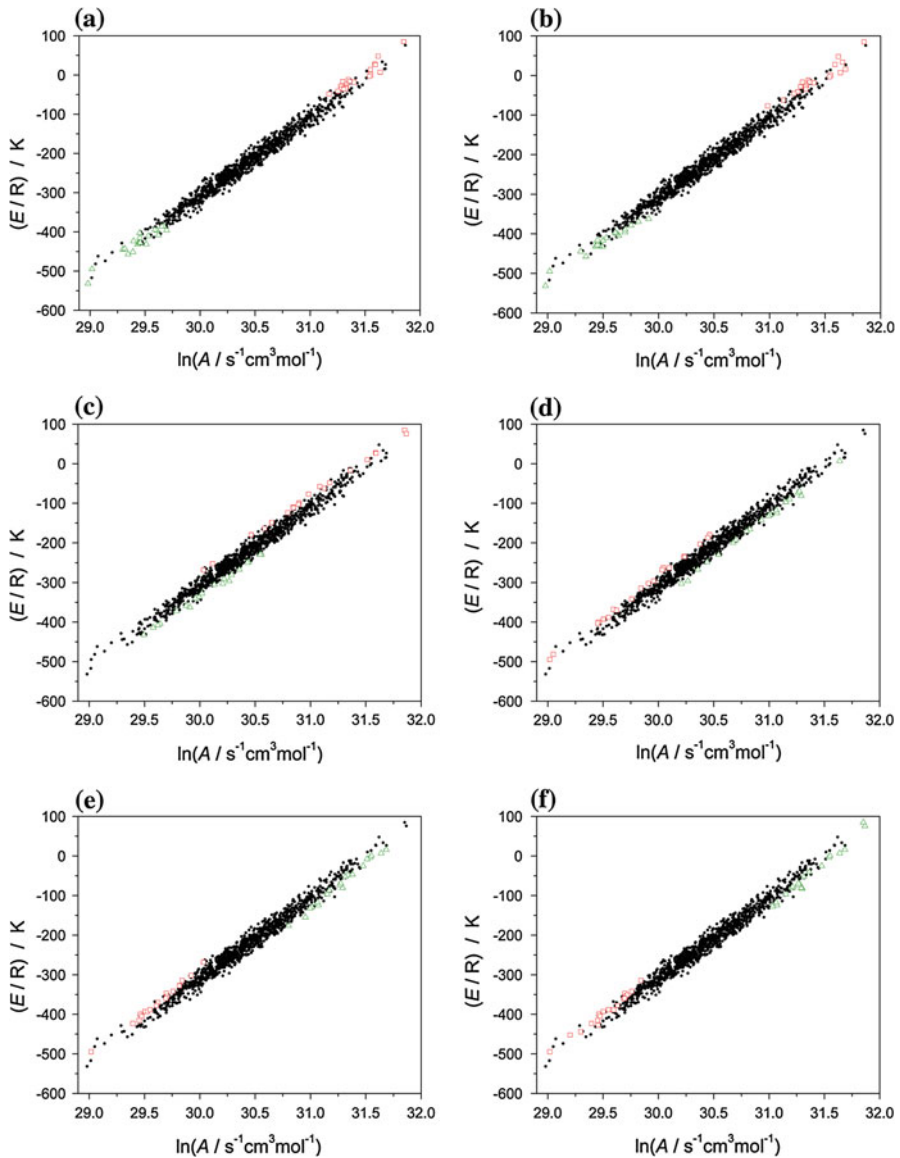
Fig. 7 1,000 random ($\ln A$, E/R) pairs of Arrhenius parameters (solid points) of reaction R2. The triangles and the squares correspond to the low and high $\ln k$ values having each less than 2% probability, respectively, at each indicated temperature (see text) **a** $T = 220$ K. **b** $T = 450$ K. **c** $T = 700$ K. **d** $T = 800$ K. **e** $T = 900$ K. **f** $T = 1,000$ K

always on the opposite edges of the 2D distribution, but their location changes with temperature. These points make a half rotation while the temperature changes from 220 K to 1,000 K. Comparison of Fig. 7a and f shows that the same ($\ln A$, E/R) points may belong to small and large $\ln k$ values (compared to the mean value) both having low-probability, depending on temperature.

5 Conclusions

Uncertainty analysis of chemical kinetic models became an important issue in the last years (see *e.g.* [3–10,22,23]), since agreement between experimental and simulated data can be judged only if the uncertainty of both is known. A contradiction in the chemical kinetics databases (see *e.g.* [2]) is that the rates of reactions are characterized by Arrhenius parameters, but the uncertainties of these Arrhenius parameters are not provided. Instead, the uncertainties of the rate parameters are indicated in the whole temperature range using a generally temperature dependent uncertainty parameter f.

In this article, the results of a series of numerical investigations are reported on the examples of reactions R1: $H + H_2O_2 = HO_2 + H_2$ and R2: $O + HO_2 = OH + O_2$. The same calculations were repeated with the data of several other reactions and qualitatively similar results were obtained. Although these are important combustion reactions and up-to-date chemical kinetic data were used for these reactions, we considered that not the numerical results belonging to the actual reactions were interesting, but the general conclusions.

Our numerical studies indicated that if both transformed Arrhenius parameters ln A and E/R have uncertainty and the uncertainty parameter of k is identical at the two ends of the temperature interval, then the uncertainty parameter of k that is consistent with the uncertainty of the Arrhenius parameters should be smaller at mid temperatures. The case of temperature independent uncertainty parameter f corresponds to the case when E/R is known without uncertainty, which is a physically not realistic assumption.

It is a common situation in chemical kinetics that the rate coefficient of a reaction is well known at room temperature, while it is less studied at high temperatures. In other words, the rate coefficient is known with low uncertainty (small variance, low uncertainty parameter f) at room temperature, while the uncertainty of k is high at high temperature that corresponds to large variance and large uncertainty parameter f.

A numerical algorithm is suggested that is applicable when uncertainty parameters f_1 and $f_2(f_1 < f_2)$ are defined at temperatures T_1 and T_2. The method provides the corresponding random (ln A, E/R) points and the distribution of these points can be represented by a 2D histogram. Using this histogram, the joint probability density function (*pdf*) of the Arrhenius parameters can be estimated. All calculations were carried out with custom made Matlab codes.

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