Uncertainty of the Arrhenius parameters of important elementary reactions of the hydrogen–oxygen system

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Abstract

For several important elementary reactions of the H/O system, all available *k* measurements and theoretical determinations were plotted; $k_{\min}(T)$ and $k_{\max}(T)$ limits were determined within a range of temperature. These *k* limits were used to obtain temperature dependent uncertainty parameter $f(T)$ and to determine the covariance matrix of the Arrhenius parameters. The procedure was carried out for reactions $H+O_2+M=HO_2+M$, $HO_2+H=H_2+O_2$, $OH+H_2=H_2O+H$, $H+O_2=O+OH$, $O+H_2=H+OH$, $H_2O_2+H=H_2+HO_2$, $OH+OH=H_2O+O$ and $H+HO_2=OH+OH$.

Introduction

Chemical kinetics databases for many elementary gas-phase reactions provide the recommended values of the Arrhenius parameters, the temperature range of their validity and the temperature dependence of the uncertainty of rate coefficient *k*. The latter is defined by uncertainty parameter *f*. However, the uncertainty parameter is frequently considered to be temperature independent, which implies that only Arrhenius parameter *A* has uncertainty and the values of Arrhenius parameters *n* and *E* are assumed to be known without uncertainty [1]. This unrealistic conclusion can be avoided by using appropriate $f(T)$ functions, but such functions are not available from the databases.

The aim of this work is to find $f(T)$ uncertainty functions that are in accordance with the results of all available direct measurements and theoretical calculations for the corresponding reactions. Also, the covariance matrix of the Arrhenius parameters was determined from the obtained uncertainty function. The covariance matrix defines the 3D domain of uncertainty of the Arrhenius parameters [1].

Uncertainty of the rate coefficients

Data collections containing the rate parameters of gas phase elementary reactions characterize the uncertainty of the rate coefficient with a single temperature dependent value. Uncertainty parameter *f* is defined in the following way:

$$f = \log_{10}\left(k^0/k_{\min}\right) = \log_{10}\left(k_{\max}/k^0\right) \qquad (1)$$

where k^0 is the recommended (most probable) value of the rate coefficient, $k_{\min}$ and $k_{\max}$ are the extreme, but still not excludable values. According to this assumption, the upper and lower extreme values differ from the recommended value by a multiplication factor, which means that on a logarithmic scale the extreme values are located symmetrically around the recommended value. Assuming that the minimum and maximum values of the rate coefficients correspond to 3σ deviations [2–7] or 2σ deviations [8–9] from the recommended value on a logarithmic scale, the uncertainty parameter *f* can be converted [3] at a given temperature *T* to the variance of the logarithm of the rate coefficient:

$$\sigma^2(\ln\{k\}) = \left((f \cdot \ln 10)/\mu\right)^2 \qquad (2)$$

where $\mu = 3$ or 2.

The temperature dependence of the rate coefficient *k* can be described by the modified Arrhenius equation $k = A\ \{T\}^n \exp(-E/RT)$. Operator { } results in the dimensionless value of a physical quantity at known units. Introducing transformed parameters $\kappa(T) := \ln\{k(T)\}$, $\alpha := \ln\{A\}$ and $\varepsilon := \ln\{E\}$, the linearized form of the modified Arrhenius equation is

$$\kappa(T) = \alpha + n\ln\{T\} - \varepsilon T^{-1} \qquad (3)$$

The temperature dependent rate coefficient $k(T)$ (and its logarithm $\kappa(T)$) can be considered a random variable deduced from measurements and calculations [1]. Transformed Arrhenius parameters α, *n*, and ε are also random values, since these can be calculated from the random values of $\kappa(T)$ given at three temperatures using the linearized Arrhenius equation (3). The joint probability density function of the Arrhenius parameters is independent of temperature. This means that all central moments are also independent of temperature, including their expected values ($\bar{\alpha}$, $\bar{n}$, $\bar{\varepsilon}$), variances ($\sigma_\alpha^2, \sigma_n^2, \sigma_\varepsilon^2$) and correlations ($r_{\alpha n}$, $r_{\alpha\varepsilon}$, $r_{\varepsilon n}$). According to the definition of variances and correlation coefficients, the following relations are valid:

$$\begin{gathered} 0 \le \sigma_\alpha, \sigma_n, \sigma_\varepsilon \\ -1 \le r_{\alpha n}, r_{\alpha\varepsilon}, r_{n\varepsilon} \le +1 \end{gathered} \qquad (4)$$

$$0 \le 1 - r_{\alpha n}^2 - r_{\alpha\varepsilon}^2 - r_{n\varepsilon}^2 + 2 r_{\alpha n}\, r_{\alpha\varepsilon}\, r_{n\varepsilon} \qquad (5)$$

Denote $\bar{\kappa}(T)$ the expected value and $\sigma_\kappa^2(T)$ the variance of κ at a given temperature $T \in [T_1, T_2]$. As a consequence of equation (3), equation (6) is valid for the expected values of random variables $\kappa(T)$, α, *n*, and ε.

$$\bar{\kappa}(T) = \bar{\alpha} + \bar{n}\ln\{T\} - \bar{\varepsilon}\, T^{-1} \qquad (6)$$

In our previous work [1], the following relation was deduced between the variance of $\kappa(T)$ and the elements of the covariance matrix of the transformed Arrhenius parameters:

$$\begin{aligned}\sigma_{\kappa}^{2}(T) = {} & \sigma_{\alpha}^{2} + \sigma_{n}^{2}\ln^{2}\{T\} + \sigma_{\varepsilon}^{2}T^{-2} \\ & + 2r_{\alpha n}\sigma_{\alpha}\sigma_{n}\ln\{T\} - 2r_{\alpha\varepsilon}\sigma_{\alpha}\sigma_{\varepsilon}T^{-1} \\ & - 2r_{n\varepsilon}\sigma_{n}\sigma_{\varepsilon}T^{-1}\ln\{T\}\end{aligned} \tag{7}$$

Also, a method was developed [1] for the determination of the covariance matrix of the Arrhenius parameters by fitting equation (7) to uncertainty data of the rate coefficient at various temperatures by taking also into account relations (4) and (5). For the three-parameter Arrhenius expression to determine the elements of the covariance matrix, uncertainty of the rate coefficient has to be known at least at six different temperatures. A 3D domain of uncertainty can be determined by the covariance matrix of the Arrhenius parameters [1].

In this work the same fitting procedure is applied, but instead of fitting to uncertainty data taken from chemical kinetics databases, the uncertainty function defined by equations (2) and (7) is fitted to empirical uncertainty values obtained from the scatter of literature data. The software tool used for the fitting has been developed earlier [1] and it is available from our Web site [10].

Uncertainty of the rate coefficient of the reverse reaction

If the Arrhenius parameters of the forward reaction are known, the rate coefficient k_{f} can be calculated for any temperature. Knowing the standard reaction enthalpy $\Delta_{\mathrm{r}}H^{\theta}$ and standard reaction entropy $\Delta_{\mathrm{r}}S^{\theta}$ at this temperature, the standard reaction Gibbs function can be calculated:

$$\Delta_{\mathrm{r}}G^{\theta} = \Delta_{\mathrm{r}}H^{\theta} - T\,\Delta_{\mathrm{r}}S^{\theta} \tag{8}$$

For ideal gases the equilibrium constant K_p expressed in normalized pressures p/p^{θ} can be calculated from the standard reaction Gibbs function:

$$\Delta_{\mathrm{r}}G^{\theta} = -RT\ln K_p \tag{9}$$

where p^{θ} is the standard pressure 1 bar and coefficients ν_{i} are the stoichiometric coefficients. The next step is the calculation of the equilibrium constant expressed in concentrations K_c:

$$K_c = K_p\,\left(p^{\theta}/RT\right)^{\sum\nu_{\mathrm{i}}} \tag{10}$$

The rate coefficient of the backward reaction k_{b} can be calculated from rate coefficient of the forward reaction k_{f} and the equilibrium constant K_c:

$$k_{\mathrm{b}} = k_{\mathrm{f}}/K_c \tag{11}$$

Combining equations (8) to (11) and taking the natural logarithm of both sides gives the following equation:

$$\ln k_{\mathrm{b}} = \ln k_{\mathrm{f}} + \Delta_{\mathrm{r}}H^{\theta}/RT - \Delta_{\mathrm{r}}S^{\theta}/R - \left(\sum\nu_{\mathrm{i}}\right)\ln\left(p^{\theta}/RT\right) \tag{12}$$

At a given temperature T, term p^{θ}/RT has zero uncertainty. The standard reaction entropy can be calculated with high accuracy; therefore, the uncertainty of the corresponding term is also negligible. Both forward rate coefficient k_{f} and standard reaction enthalpy $\Delta_{\mathrm{r}}H^{\theta}$ have relatively high uncertainty and these uncertainties can be considered to be uncorrelated. This means that the variance of rate coefficient k_{b} can be calculated in the following way:

$$\sigma^{2}(\ln k_{\mathrm{b}}) = \sigma^{2}(\ln k_{\mathrm{f}}) + (1/RT)^{2}\sigma^{2}\left(\Delta_{\mathrm{r}}H^{\theta}\right) \tag{13}$$

The reaction enthalpy can be calculated as the linear combination of the standard enthalpies of formation of the participating species.

$$\Delta_{\mathrm{r}}H^{\theta} = \mathbf{v}^{\mathrm{T}}\boldsymbol{\Delta}\mathbf{H}_{\mathrm{f}}^{\theta} = \boldsymbol{\Delta}\mathbf{H}_{\mathrm{f}}^{\theta\mathrm{T}}\ \mathbf{v} \tag{14}$$

Here $\mathbf{v}$ and $\boldsymbol{\Delta}\mathbf{H}_{\mathrm{f}}$ are the column vectors of stoichiometric coefficients and the standard enthalpies of formation, respectively. The variance of the reaction enthalpy can be calculated from the covariance matrix of the standard enthalpies of formation of the participating species.

$$\sigma^{2}\left(\Delta_{\mathrm{r}}H^{\theta}\right) = \mathbf{v}^{\mathrm{T}}\,\overline{(\boldsymbol{\Delta}\mathbf{H}_{\mathrm{f}}^{\theta} - \overline{\boldsymbol{\Delta}\mathbf{H}_{\mathrm{f}}^{\theta}})(\boldsymbol{\Delta}\mathbf{H}_{\mathrm{f}}^{\theta} - \overline{\boldsymbol{\Delta}\mathbf{H}_{\mathrm{f}}^{\theta}})^{\mathrm{T}}}\,\mathbf{v} = \mathbf{v}^{\mathrm{T}}\ \boldsymbol{\Sigma}_{\Delta H}\mathbf{v} \tag{15}$$

Here $\boldsymbol{\Sigma}_{\Delta H}$ is the covariance matrix of the standard enthalpies of formation. For example, for reaction A + B → C + D the variance of the reaction enthalpy can be calculated in the following way:

$$\begin{aligned}\sigma^{2}\left(\Delta_{\mathrm{r}}H^{\theta}\right) = {} & \\ & \sigma^{2}\left(\Delta H_{\mathrm{f\,A}}^{\theta}\right) + \sigma^{2}\left(\Delta H_{\mathrm{f\,B}}^{\theta}\right) + \sigma^{2}\left(\Delta H_{\mathrm{f\,C}}^{\theta}\right) + \sigma^{2}\left(\Delta H_{\mathrm{f\,D}}^{\theta}\right) \\ & + 2r_{\mathrm{AB}}\sigma\left(\Delta H_{\mathrm{f\,A}}^{\theta}\right)\sigma\left(\Delta H_{\mathrm{f\,B}}^{\theta}\right) + 2r_{\mathrm{CD}}\sigma\left(\Delta H_{\mathrm{f\,C}}^{\theta}\right)\sigma\left(\Delta H_{\mathrm{f\,D}}^{\theta}\right) \\ & - 2r_{\mathrm{AC}}\sigma\left(\Delta H_{\mathrm{f\,A}}^{\theta}\right)\sigma\left(\Delta H_{\mathrm{f\,C}}^{\theta}\right) - 2r_{\mathrm{AD}}\sigma\left(\Delta H_{\mathrm{f\,A}}^{\theta}\right)\sigma\left(\Delta H_{\mathrm{f\,D}}^{\theta}\right) \\ & - 2r_{\mathrm{BC}}\sigma\left(\Delta H_{\mathrm{f\,B}}^{\theta}\right)\sigma\left(\Delta H_{\mathrm{f\,C}}^{\theta}\right) - 2r_{\mathrm{BD}}\sigma\left(\Delta H_{\mathrm{f\,B}}^{\theta}\right)\sigma\left(\Delta H_{\mathrm{f\,D}}^{\theta}\right)\end{aligned} \tag{16}$$

where $\sigma(\Delta H_{\mathrm{f\,i}}^{\theta})$ is the standard deviation of the enthalpy of formation of the i-th species, and r_{jk} is the correlation coefficient between the standard enthalpies of formation of species j and k. The thermodynamic databases contain only the standard deviations of the enthalpies of formation of the species. However, the Active Table approach [11] (ATcT) and the NEAT method [12] also provide information about the correlation of the enthalpies of formation.

It is frequently assumed that the enthalpies of formation and the $\ln k_{\mathrm{f}}$ values have normal distribution. Any linear function of normally distributed random variables also follows a normal distribution, therefore $\ln k_{\mathrm{b}}$ will also be normally distributed.

Determination of the temperature dependent uncertainty parameter

The following algorithm was elaborated for the determination of the temperature dependent uncertainty range of the rate coefficient of an elementary gas phase reaction.

1. Using the NIST Chemical Kinetics Database [13], data for the experimental and theoretical determinations of the rate coefficients were collected for both directions of the elementary

reaction. Direction associated with more information was considered as the forward one.

2. The rate parameters of the backward reactions were converted to the rate parameters of the forward reactions using equation (12). These two sets of rate parameters were used together to determine the scatter of the literature data.
3. A mean rate coefficient – temperature function $k_{\mathrm{mean}}(T)$ was selected and a temperature dependent $f(T)$ function was defined in such a way that all experimentally determined or theoretically calculated $k(T)$ functions remained within values k_{min} and k_{max}. These uncertainty limits were symmetrical on a logarithmic scale:

$$\ln k_{\mathrm{min}} = \ln k_{\mathrm{mean}} - f \quad \text{and} \quad \ln k_{\mathrm{max}} = \ln k_{\mathrm{mean}} + f \qquad (17)$$

4. The $f(T)$ function was tabulated at every 100 K temperature and based on the method developed in our previous work [1] the elements of the covariance matrix of the Arrhenius parameters were determined by fitting equation (7) to these uncertainty data points while considering constraints in equations (4) and (5). Using equations (7), (2) and (1), the $f(T)$ function was calculated using μ=3 from the covariance matrix of the Arrhenius parameters.

Reaction R1: H + O_2 + M → HO_2 + M

This is the most important chain termination reaction step of hydrogen combustion. In most measurements belonging to this elementary reaction, argon or nitrogen was used as bath gas (M = Ar or N_2). The low-pressure limit forward reaction has been measured by several authors, but no measured rate coefficient was found for the backward reaction.

Table 1: Arrhenius parameters (low-pressure limit) recommended for reaction H + O_2 + M → HO_2 + M. The units are $\mathrm{cm^6 mol^{-2} s^{-1}}$ for A and K for E/R.

Ó Conaire *et al.* [14], bath gas N_2 A= $3.482 \cdot 10^{16}$, $n = -0.41$, $E/R = -561.5$ Temperature range 298 – 3000 K.
Konnov [15], bath gas N_2 A= $5.70 \cdot 10^{19}$, $n = -1.4$, $E/R = 0$ Temperature range 300 – 2000 K.
Konnov [15], bath gas Ar A= $7.43 \cdot 10^{18}$, $n = -1.2$, $E/R = 0$ Temperature range 300 – 2000 K.
Baulch *et al.* [16], bath gas N_2 A= $2.65 \cdot 10^{19}$, $n = -1.4$, $E/R = 0$ Temperature range 298 – 2000 K.
Baulch *et al.* [16], bath gas Ar A= $6.9 \cdot 10^{18}$, $n = -1.2$, $E/R = 0$ Temperature range 298 – 2000 K.
Hong *et al.* [17], bath gas N_2 A= $2.65 \cdot 10^{19}$, $n = -1.3$, $E/R = 0$
Hong *et al.* [17], bath gas Ar A= $6.81 \cdot 10^{18}$, $n = -1.2$, $E/R = 0$

Table 1 contains the rate coefficients of these reactions as recommended by Ó Conaire *et al.* [14], Konnov [15], Baulch *et al.* [16], and Hong *et al.* [17]

Two Arrhenius plots, one for nitrogen and one for argon bath gas, were created for the temperature dependence of the rate coefficient (low-pressure limit) for reaction H+O_2+M→HO_2+M. All data entries of the NIST Chemical Kinetics database[13] were used and therefore these figures contained experimentally measured and theoretically calculated rate coefficients, and also values recommended in reviews. In the next step, the plots belonging to the rate parameters listed in reviews and too obsolete measurements were deleted. The measurements were checked one-by-one and all measurements that were considered as obsolete had turned out to be done before 1970. The revised plots are shown in Figure 1 and Figure 2 for nitrogen and argon bath gases, respectively. The thick red line in both figures corresponds to the Baulch *et al.* [16] recommendations.

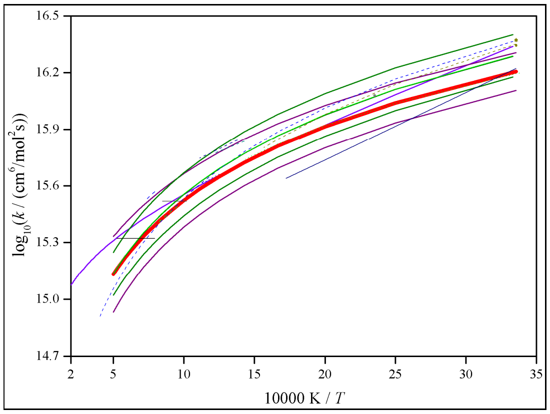

Figure 1. Arrhenius plots of selected measured and calculated rate coefficients for reaction H+O_2+M→ HO_2 +M (low-pressure limit) in nitrogen bath gas.

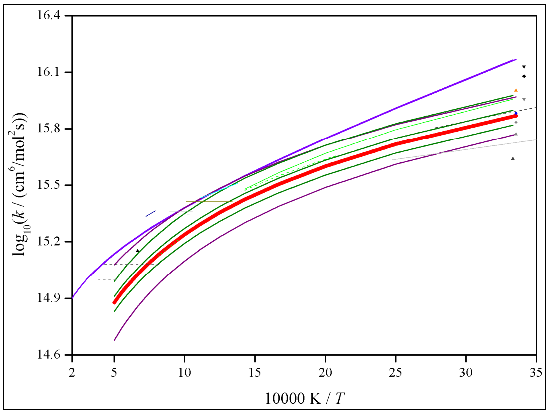

Figure 2. Arrhenius plots of selected measured and calculated rate coefficients for reaction H+O_2+M→ HO_2+M (low-pressure limit) in argon bath gas.

Ó Conaire *et al.* [14] provided data for M=N_2 and recommended third body efficiency m=0.67 for argon. Konnov, Baulch *et al.* and Hong *et al.* recommended different Arrhenius parameters for bath gases nitrogen and argon. Calculating the rate coefficient from these recommendations at many temperatures for both bulk gases and taking the ratio of the two, $m = k_{Ar}/k_{N2}$, the third body efficiency (argon relative to nitrogen) changes between 0.46 and 0.56 in temperature range 300–2000 K. In combustion systems this reaction is important in the range of 900–1400 K, where m=0.51–0.54. Comparing Figures 1 and 2, we found a good overlap of the determined rate coefficients if the rate coefficients obtained for nitrogen were used and the results for argon were scaled assuming m= 0.5.

Figure 3 shows the rate parameters in an Arrhenius plot when the bath gas is nitrogen. Uncertainty values f_i were determined at every 100 K in such a way that the obtained k_{min} and k_{max} values provided a lower and an upper limit for all the suggested rate coefficient values. A similar figure was created for argon (see Figure 4) by multiplying the mean function obtained for nitrogen by m=0.5 and the same f_i values were used. It is clear that the k_{max} and k_{min} values obtained this way also provide an upper and lower limit for all the suggested rate coefficient values for argon bath gas.

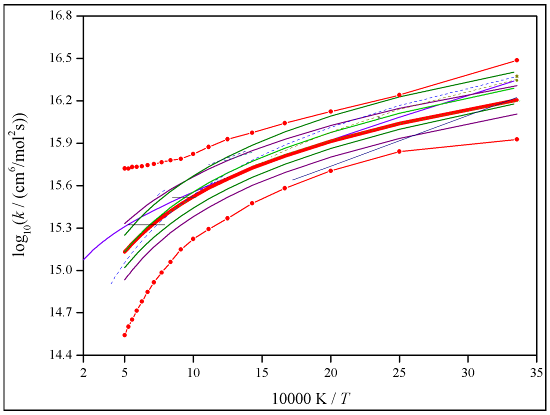

Figure 3. Upper and lower uncertainty limits (dots and solid line) for reaction R1 in nitrogen bath gas.

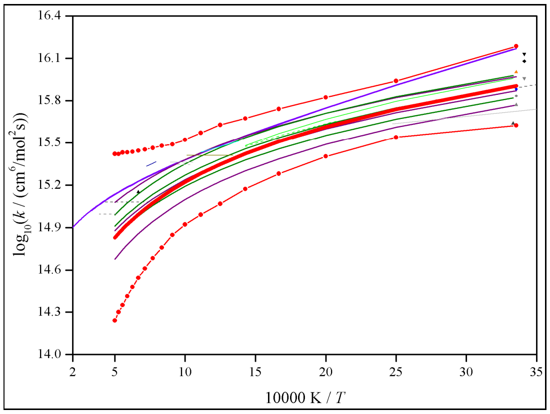

Figure 4. Upper and lower uncertainty limits (dots and solid line) for reaction R1 in argon bath gas.

Figure 5 shows the uncertainty parameters f_i that were determined at every 100 K from 300 K to 2000 K and function $f(T)$ fitted to this curve using equations (2) and (7). The obtained parameters of the covariance matrix of the transformed Arrhenius parameters were the following: $\sigma(\ln\{A\})$= 5.018, $\sigma(n)$= 0.685, $\sigma(E/R)$= 389.9 K, $r(\ln\{A\}, n)$= –0.99869, $r(\ln\{A\}, E/R)$= 0.99750, and $r(n, E/R)$= –0.99256.

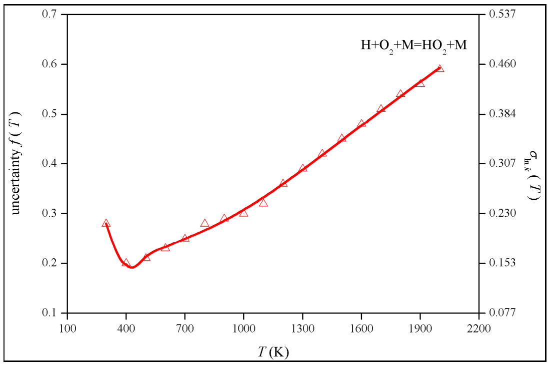

Figure 5. Uncertainty parameters f_i (triangles) as deduced from Figures 3 and 4, and the curve (solid line) fitted to these points using equation (7) and relations (4) and (5).

The rate parameters of reverse reaction $HO_2+M \rightarrow H+O_2+M$ (bath gas nitrogen) were determined by program MECHMOD from the rate parameters of the forward reaction, as recommended by Baulch *et al.* The low-pressure limit Arrhenius parameters are $\ln\{A\}$ = 45.05, n = –1.32 and E/R = 24576 K. Numerical value of A corresponds to units cm, mol, s. No experimental or theoretical determination for this reaction was found in the NIST Chemical Kinetics Database.

For the case of this reaction, the uncertainty of the thermodynamic data is very low, therefore uncertainty of the backward reaction can be considered to be equal to the uncertainty of the forward reaction.

Results

The procedure above was repeated for a series of elementary reactions, important at the combustion of H/O systems. The temperature dependent uncertainty determined from the scatter of literature data and the fitted theoretical uncertainty curves (according to equations (2) and (7)) are shown in Figure 6 for each investigated reaction. The results are summarized in Table 2.

The excellent agreement between the fitted curve and the data shows the strength and flexibility of the formula [1] to describe the temperature dependence of uncertainty determined from the scatter of literature data.

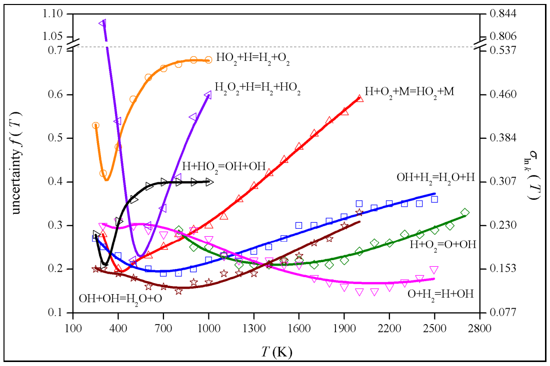

Figure 6. Uncertainty parameters f_i obtained from the scatter of literature data and the curves (solid line) fitted to these points using equation (7) and relations (4) and (5) for each investigated reaction.

Table 2. The mean Arrhenius parameters and their standard deviations and correlations. Numerical values ({ }) of physical quantities correspond to units cm, mol, s, K. The temperature ranges of validity and the range of uncertainty values are also indicated.

$H+O_2+M=HO_2+M$ low-pressure limit	$\alpha = \ln\{A\}$	N	$\varepsilon = E/R$
	44.72	−1.30	0
	σ_α	σ_n	σ_ε
	5.018	0.685	389.9
	$r_{\alpha n}$	$r_{\alpha\varepsilon}$	$r_{n\varepsilon}$
	−0.99869	0.99750	−0.99256
	Range of temperature: 298 – 2000 K		
	Range of uncertainty: f=0.20 – 0.59		

$HO_2+H=H_2+O_2$	$\alpha = \ln\{A\}$	n	$\varepsilon = E/R$
	18.03	1.77	−286
	σ_α	σ_n	σ_ε
	5.666	0.710	515.4
	$r_{\alpha n}$	$R_{\alpha\varepsilon}$	$r_{n\varepsilon}$
	−0.99538	0.99889	−0.98976
	Range of temperature: 250 – 1000 K		
	Range of uncertainty: f=0.42 – 0.68		

$OH+H_2=H_2O+H$	$\alpha = \ln\{A\}$	n	$\varepsilon = E/R$
	19.2	1.52	1740
	σ_α	σ_n	σ_ε
	1.392	0.207	22.95
	$r_{\alpha n}$	$R_{\alpha\varepsilon}$	$r_{n\varepsilon}$
	−0.99403	0.999377	−0.99726
	Range of temperature: 250 – 2500 K		
	Range of uncertainty: f=0.19 – 0.36		

$H+O_2=O+OH$	$\alpha = \ln\{A\}$	n	$\varepsilon = E/R$
	32.97	-0.097	7560
	σ_α	σ_n	σ_ε
	4.622	0.581	675.7
	$r_{\alpha n}$	$r_{\alpha\varepsilon}$	$r_{n\varepsilon}$
	−0.999852	0.98788	−0.99041
	Range of temperature: 800 – 2700 K		
	Range of uncertainty: f=0.21 – 0.33		

$O+H_2=H+OH$	$\alpha = \ln\{A\}$	n	$\varepsilon = E/R$
	10.82	2.67	3167
	σ_α	σ_n	σ_ε
	2.956	0.369	241.5
	$r_{\alpha n}$	$r_{\alpha\varepsilon}$	$r_{n\varepsilon}$
	−0.99816	0.91356	−0.88721
	Range of temperature: 297 – 2495 K		
	Range of uncertainty: f=0.15 – 0.30		

$H_2O_2+H=H_2+HO_2$	$\alpha = \ln\{A\}$	n	$\varepsilon = E/R$
	28.16	0	1890
	σ_α	σ_n	σ_ε
	6.433	0.845	721.1
	$r_{\alpha n}$	$r_{\alpha\varepsilon}$	$r_{n\varepsilon}$
	−0.98759	0.75415	−0.64164
	Range of temperature: 300 – 1000 K		
	Range of uncertainty: f=0.22 – 1.08		

$OH+OH=H_2O+O$	$\alpha = \ln\{A\}$	n	$\varepsilon = E/R$
	10.42	2.42	−970
	σ_α	σ_n	σ_ε
	2.564	0.351	143.6
	$r_{\alpha n}$	$r_{\alpha\varepsilon}$	$r_{n\varepsilon}$
	−0.99698	0.89714	−0.86015
	Range of temperature: 250 – 2000 K		
	Range of uncertainty: f=0.15 – 0.33		

$H+HO_2=OH+OH$	$\alpha = \ln\{A\}$	n	$\varepsilon = E/R$
	26.12	0.88	32.47
	σ_α	σ_n	σ_ε
	5.844	0.778	434.3
	$r_{\alpha n}$	$r_{\alpha\varepsilon}$	$r_{n\varepsilon}$
	−0.99800	0.99657	−0.98934
	Range of temperature: 250 – 1000 K		
	Range of uncertainty: f=0.21 – 0.40		

Conclusions

A methodology was developed for the determination of the domain of uncertainty of the Arrhenius parameters of gas phase elementary reactions. First, temperature dependent $k_{\min}$ and $k_{\max}$ values were selected in such a way that these values provide a lower and an upper limit, respectively, of all recent measurements and theoretical determinations. Selecting a mean rate coefficient – temperature function, the limits could be converted to uncertainty parameters f_i defined at a series of temperatures values T_i. The elements of the covariance matrix of the Arrhenius parameters were fitted to these uncertainty parameter values.

The procedure was carried out for 8 important reactions of the H/O system. For each elementary reaction, a 3D domain of uncertainty of the Arrhenius parameters can be defined by the covariance matrix. This can be considered as a domain which includes the „true" values of the corresponding Arrhenius parameters with very high probability.

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