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Uncertainty analysis of varying temperature chemical kinetic systems

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Abstract

All uncertainty analysis studies carried out so far on chemical kinetic systems assumed that the uncertainties of the rate coefficients are independent of temperature, which leads to wrong results in varying temperature systems. Most chemical kinetic databases provide the recommended values of the Arrhenius parameters, the temperature range of validity and the temperature dependence of the uncertainty of rate coefficient k. A method is presented for the transformation of the uncertainty of k to the joint probability density function of the Arrhenius parameters, which is needed for a realistic uncertainty analysis in varying temperature chemical kinetic systems. Recommendations are given for an improved representation of the uncertainty information in future chemical kinetic databases.

Keywords: chemical kinetics; kinetic databases; Arrhenius parameters; uncertainty analysis

1. Main text

The rate parameters in chemical kinetic systems are always determined with some uncertainty in either experiments or theoretical calculations. The temperature dependence of the rate coefficient k is given in the form of the extended Arrhenius expression, $k = AT^n \exp(-E/RT)$. By introducing the transformed rate coefficient $\kappa := \ln k$, and the transformed Arrhenius parameters $\alpha := \ln A$, and $\varepsilon := E/R$, the extended Arrhenius equation can be written in the following form:

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

In most gas kinetics databases, like in the evaluation of Baulch et al. (2005), the uncertainty of a rate coefficient is defined by temperature dependent value f in the following way:

$$f(T) = \log_{10}\left(k^0(T)/k^{\min}(T)\right) = \log_{10}\left(k^{\max}(T)/k^0(T)\right) \tag{2}$$

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 at temperature T; rate coefficients outside the $[k^{\min}, k^{\max}]$ interval are considered very improbable by the evaluators. The Arrhenius parameters provided and the uncertainty information is valid in the temperature range of (T_1, T_2).

In all uncertainty analysis studies, carried out on varying temperature systems (see *e.g.* the works of Turányi *et al.* (2002), Zádor *et al.* (2005), and Zsély *et al.* (2008)), the uncertainty of rate coefficient k was considered to be identical to the uncertainty of Arrhenius parameter A. To provide a conservative estimation, usually the largest uncertainty factor f in the temperature interval was considered, but this uncertainty was handled as a temperature independent value. Assuming that the probability density function (*pdf*) of $\kappa(T) = \ln k(T)$ at any temperature is of normal distribution truncated at $\pm 3\sigma$, the variance of rate coefficient κ can be calculated:

$$\sigma_\kappa(T) = (\ln 10/3)\, f(T) \tag{3}$$

We have shown (see Nagy and Turányi, 2010) that the following relation exists between the temperature dependent square of variance of κ and the temperature independent variances of the transformed Arrhenius parameters:

$$\sigma_\kappa^2(T) = \sigma_\alpha^2 + \sigma_n^2 \ln^2 T + \sigma_\varepsilon^2 T^{-2} + 2r_{\alpha n}\sigma_\alpha\sigma_n \ln T - 2r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon T^{-1} - 2r_{n\varepsilon}\sigma_n\sigma_\varepsilon T^{-1} \ln T \tag{4}$$

This means that if $\sigma_\kappa(T)$ is known at least at 6 temperatures, the variances ($\sigma_\alpha, \sigma_n, \sigma_\varepsilon$) and the correlation coefficients ($r_{\alpha n}, r_{\alpha\varepsilon}, r_{n\varepsilon}$) of the modified Arrhenius parameters can be calculated, by taking into account also the following conditions: $0 \le \sigma_\alpha, \sigma_n, \sigma_\varepsilon$, $-1 \le r_{\alpha n}, r_{\alpha\varepsilon}, r_{n\varepsilon} \le +1$ and $0 \le 1 - r_{\alpha n}^2 - r_{\alpha\varepsilon}^2 - r_{n\varepsilon}^2 + 2r_{\alpha n}r_{\alpha\varepsilon}r_{n\varepsilon}$. Derivation of this uncertainty information is possible only if function $\sigma_\kappa(T)$ is in accordance with an extended Arrhenius-type temperature dependence of the rate coefficient.

The approach described above has several important implications. Uncertainty analysis of varying temperature chemical kinetic systems can be carried out in a correct way knowing the joint *pdf* of the transformed Arrhenius parameters, which can be estimated from the $f(T)$ information available from the databases. It is recommended that in the future the chemical kinetic databases should contain the covariance matrix of the Arrhenius parameters instead of function $f(T)$.

The method is illustrated with the determination of the joint *pdf* of the transformed Arrhenius parameters for several elementary reactions.

2. References

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