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Uncertainty of experimental data and model parameters

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Using thermodynamics data in combustion simulations

ΔH_f ⇒ calculation of heat production in a reacting mixture

→ calculation of temperature changes

⇒ calculation of $\Delta_r G^\Theta$

c_p ⇒ calculation of temperature changes

S_m ⇒ calculation of $\Delta_r G^\Theta = \Delta_r H^\Theta - T\Delta_r S^\Theta$

→ calculation of the equilibrium constant

→ calculation of the rate coefficient of reverse reactions

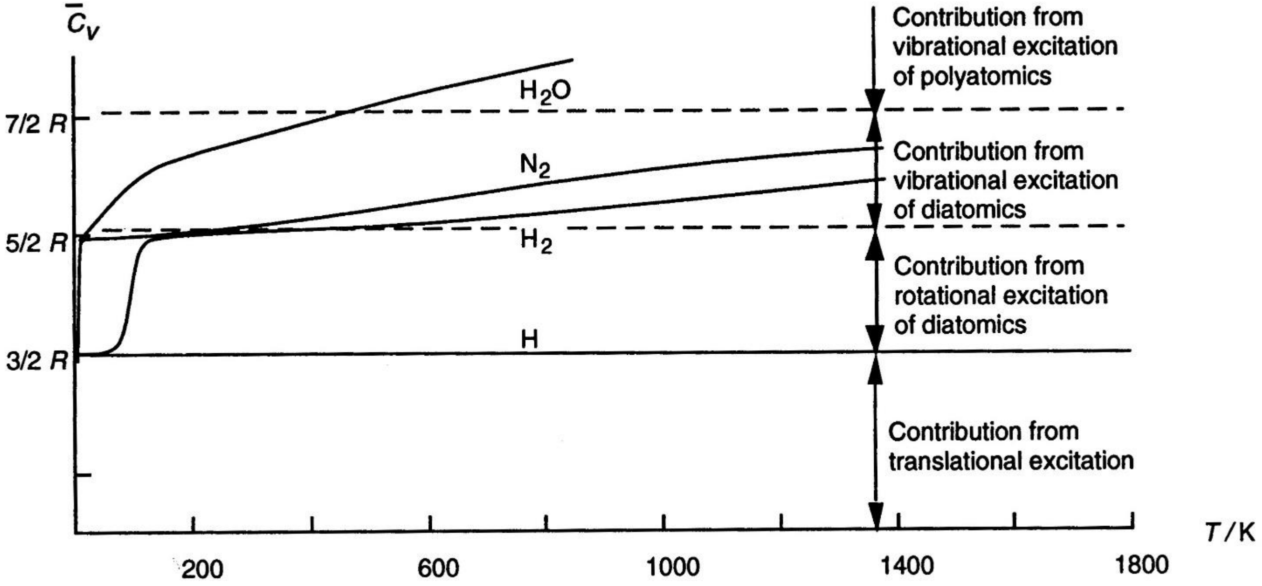
Temperature dependence of thermodynamic data

NASA polynomials

$$\frac{H^{\theta}}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$$

$$\frac{c_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$\frac{S^{\theta}}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7$$



Uncertainty of thermodynamic data

thermodynamic data influence the reaction kinetic calculations in two ways:

- Calculated temperature
- Calculation of the rate coefficients of backward reaction steps

Thermodynamic data used:

- heat capacity (can be calculated using statistical thermodynamics)
- entropy (can be calculated using statistical thermodynamics)
- standard enthalpy of formation (measurement or high level calculation)

↓

- The databases contain the recommended values and variances
- Are the enthalpies of formation correlated?

Uncertainty of thermodynamics data

c_p and S_m can be calculated from the IR spectrum
using methods of statistical thermodynamics

ΔH_f - can be computed using high level theoretical chemistry methods
(for small molecules only; not easy)

- can be determined experimentally by

- measuring the equilibrium constant of a reaction
  → reaction enthalpy → enthalpy of formation
- measuring ionization energy by mass spectrometry

Uncertainty of thermodynamic data 2

Typical uncertainty of ΔH_f (1σ):

molecules and small radicals: 0.1-0.5 kJ/mole

e.g. CO= 0.17 kJ/mole, CH_4= 0.4 kJ/mole, CH_3=0.4 kJ/mole

large radicals: 1.0 – 5.0 kJ/mole

e.g. HO_2= 3.35 kJ/mole, CH_2OH= 4.2 kJ/mole

less known radicals: 8-10 kJ/mole

e.g. HCCO= 8.8 kJ/mole, CH_2HCO= 9.2 kJ/mole

Most thermodynamics databases contain „uncertainty limits”, which can be interpreted as 2σ uncertainties.

Uncertainty of thermodynamic data 3

Question: Reaction enthalpy is changed by 1 kJ mole^{-1}
What is the consequence on the calculated equilibrium constant?

Answer: $\Delta_r H$ is changed by 1 kJ mol^{-1}
$\Delta_r S$ is assumed to be accurate $\Rightarrow$

$\Delta_r G = \Delta_r H - T\,\Delta_r S \quad \Rightarrow \quad \Delta_r G$ is also changed by 1 kJ mole^{-1}

$$- \Delta_r G = RT \ln K$$

$$- \Delta_r G - (- \Delta_r G') = 1 \text{ kJ mol}^{-1} = RT \ln K - RT \ln K' = RT \ln (K/K')$$

$$1000 \text{ J mole}^{-1} = 8.3145 \text{ J mole}^{-1} \text{ K}^{-1} \times 2000 \text{ K} \ln (K/K')$$

$$K/K' = 1.062$$

1 kJ mole^{-1} change in $\Delta_r H \Rightarrow$ 6.2% change of K

Determination of the enthalpies of formation

Methods for the determination of enthalpies of formation ΔH_f :

1) direct calorimetry experimental determination

   calorimetry; synthesis from reference state elements

   $H_2 + ½ O_2 = H_2O$ applicable for few compounds only

2) direct experimental determination from MS ionization energies

   applicable for few compounds only; not very accurate

3) direct theoretical calculation

   high level *ab initio* method required: accurate for small molecules only

4) traditional indirect method

   indirectly from experimentally measured reaction enthalpies $\Delta_r H^\Theta$

   determination of ΔH_f after a chain of calculations

Determination of the enthalpies of formation 2

„4) determination of ΔH_f after a chain of calculations”

- starting from directly determined ΔH_f values

$$\Delta_r H^{\theta} = \sum_j \nu_j \; H_f^{\theta}(j)$$

a) combining it with a $\Delta_r H^{\theta}$ value provides a new ΔH_f^{θ} value

$\Rightarrow$ indirectly determined ΔH_f^{θ}

b) GO TO a) until we get the required ΔH_f^{θ}

$\Rightarrow$ the chain of calculation provides the required ΔH_f^{θ}

PROBLEMS:

- Going on in the chain of calculations, the errors are accumulated ΔH_f^{θ} values at the end of a long chain are not very accurate.
- ΔH_f^{θ} values for the same species can be obtained at the ends of two different calculation chains $\Rightarrow$ different ΔH_f^{θ} values are obtained **?????**

Active Thermochemical Tables (ATcT)

Idea of Branko Ruscic (Argonne National Lab) http://atct.anl.gov/

the determination of many enthalpies of formation ΔH_f^θ in one step:

using *n* direct experimental determination: $H_f^\Theta(j) = A_j$ $j = 1, \ldots, n$

using *m* measured $\Delta_r H^\theta$ values: $\Delta_r H_i^\theta = \sum_j \nu_{ij} H_f^\Theta(j)$ $j = n+1, \ldots, n+m$

The aim is the determination of *k* values of ΔH_f^θ :

- if $k > n+m$ ⇒ not enough info
- if $k < n+m$ ⇒ overdetermined linear algebraic system of equations
  ⇒ determination of the ΔH_f^θ values by the least squares method

If the errors of the measurements are also taken into account

⇒ **weighted least squares method**

B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszevski, S. J. Bittner, S. G. Nijsure, K. A.Amin, M. Minkoff, A. F. Wagner: Introduction to Active Thermochemical Tables: Several „key" enthalpies of formation revisited. *J. Phys. Chem. A* **108**, 9979-9997 (2004)

Active Thermochemical Tables (ATcT) 2

NOTES:

The reason of the name: the original idea was that the tables would be „active”: on a Web site adding new measurement data all enthalpies of formation would be recalculated.

It never worked this way: Dr. Ruscic is continously adding new measurements and sometimes publishes $\Delta_r H^\theta$ values.

Please observe the similarity and difference between ATcT and the optimization of kinetic reaction mechanisms:

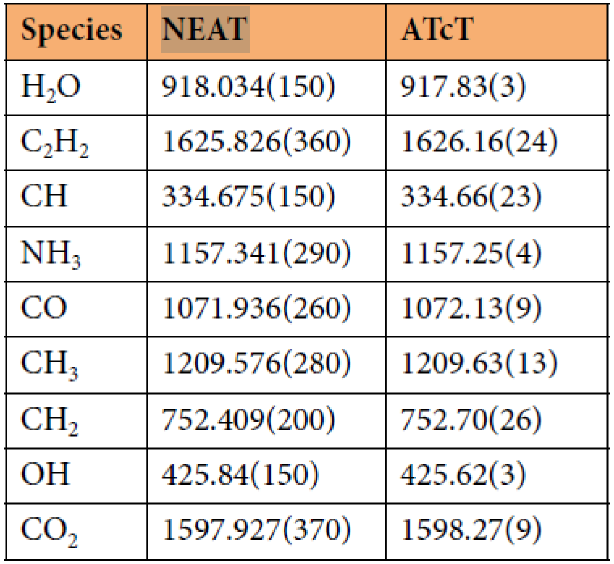
- using both direct and indirect measurements
- the error of measurements is used for the calculation of the uncertainty of parameters
- **ATcT**: the simulated data are a linear functions of the parameters

kinetics: the simulated data are obtained by solving ODEs or PDEs (strongly nonlinear functions of parameters)

B. Ruscic, R. E. Pinzon, G. von Laszewski, D. Kodeboyina, A. Burcat, D. Leahy, D. Montoya, A. F. Wagner, Active Thermochemical Tables: Thermochemistry for the 21st Century. *J. Phys. Conf. Ser.* **16**, 561-570 (2005)

Network of computed reaction enthalpies to atom-based thermochemistry (NEAT)

Quantum chemically computed 0 K reaction enthalpies are determined, and these data yield an overdetermined linear system of equations for 0 K enthalpies of formation for the species. These enthalpies are calculated using a weighted, linear least-squares approximation, providing internally consistent enthalpies of formation. Different quantum chemical approximations have different sources of error; thus, the reaction enthalpies computed this way have "random" residual errors.



Species	NEAT	ATcT
H_2O	918.034(150)	917.83(3)
C_2H_2	1625.826(360)	1626.16(24)
CH	334.675(150)	334.66(23)
NH_3	1157.341(290)	1157.25(4)
CO	1071.936(260)	1072.13(9)
CH_3	1209.576(280)	1209.63(13)
CH_2	752.409(200)	752.70(26)
OH	425.84(150)	425.62(3)
CO_2	1597.927(370)	1598.27(9)

enthalpies of formation at 0 K (kJ mol^{-1})

The ReSpecTh / Th website contains computed reaction enthalpies for 355 reactions. This dataset was used to determine 0 K enthalpies of formation for 188 species.

Császár, A. G. & Furtenbacher, T.: From a network of computed reaction enthalpies to atom-based thermochemistry (NEAT), *Chem. Eur. J.*, **16**, 4826–4835 (2010).

Internet sources of thermochemical data

Burcat's Thermodynamic Data

This database was originally published on Prof. Alexander Burcat's Technion Web site. It was continuously updated till July 2023.
The Chemkin-II thermo database was based on the Burcat collection.
ReSpecTh contains a mirror of the last version of the original site + added search services. NASA polynomials are provided!
https://respecth.elte.hu/burcat.php

NIST Chemistry WebBook

Thermochemical data for over 7000 organic and small inorganic compounds (enthalpy of formation, heat capacity, entropy)
temperature dependence: yes, NASA polynomials: no
https://webbook.nist.gov/

Caltech's Thermodynamic Data collection

Data collected from NIST-JANAF Tables, NIST Chemistry Webbook, NASA CEA (Chemical Equilibrium Computation) website,
DLR website, ANL ATcT website.
https://shepherd.caltech.edu/EDL/PublicResources/sdt/thermo

Internet sources of thermochemical data 2

Ruscic's Active Thermochemical Tables / Argonne National Laboratory

ATcT enthalpies of formation based on
version 1.220 of the Thermochemical Network (as of 03/26/2025).

0 K and 298.15 K enthalpies of formation for 3444 species.
„As opposed to traditional sequential thermochemistry, where the provenance of a given enthalpy of formation is typically a single measurement, the provenances of ATcT enthalpies of formation are obtained by analysing and solving a large Thermochemical Network"

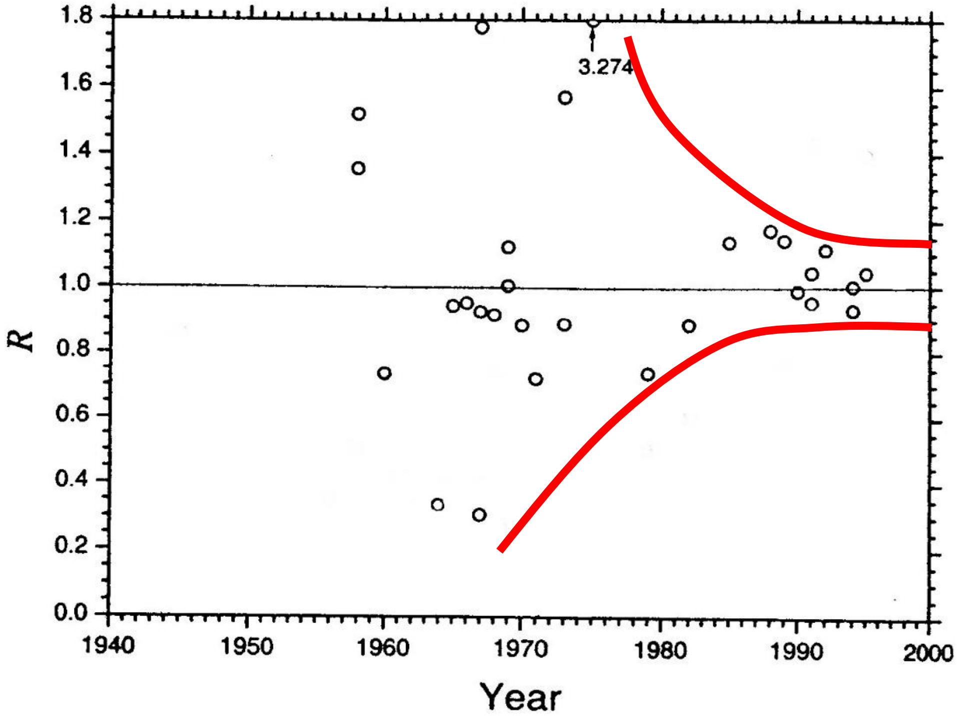
- entropy and heat capacity values are not provided
- NASA polynomials are not provided
- the covariance matrix of the enthalpies of formation is calculated, but not published (only the diagonal elements)

https://atct.anl.gov/

Few reaction rate coefficients are known

rate coefficients of about 300 reaction steps is well known
(with accuracy of about ± 30%)

although in a combustion mechanism several hundred/thousand
reaction steps are present



rate coefficient of reaction $H + O_2 \rightarrow OH + O$ *vs.* year of measurement

Why is the quantitative modelling of combustion systems possible?

- **many common reactions**

  there are many common reactions
  in the combustion mechanisms of
  basic fuels; these rate coefficents are known

- **chemical compounds with similar structures**

  if the rate coefficent is known for a given compound
  the rate coefficient for a similar compound can be estimated

- **Only a small fraction of the rate parameters determine the simulation results**

  (these parameters can be identified with sensitivity analysis)

Features of rate coefficient data

☹ many measurements only near 300 K

(atmospheric chemistry measurements,
easier to measure at room temperature,
less data at high temperature)

☹ The rate coefficients of radical recombination reactions
(*e.g.* $2\ CH_3 + M \leftrightarrow C_2H_6 + M$)
may depend on the the pressure and bath gas,
but usually few data are available for the
p and third body dependence

☹ multichannel reactions
only the rate coefficient of the overall reaction is known
for many reactions
(sum of the rate coefficients of the individual channels)
frequently the individual rate coefficients / branching ratios are not known

Multichannel reactions

example:

$H+HO_2 \rightarrow 2\ OH$ (chain branching!)

$\rightarrow H_2+O_2$ (chain termination!)

$\rightarrow H_2O+O$ (chain branching, due to the later reaction $O + H_2 \rightarrow OH + H$)

The change of branching ratio with temperature have a high influence on the rate of overall reaction

„energy barrier is not discriminative at high temperature”

low temperature:

the channel with the lowest activation energy is fast

high temperature:

no simple rule for the preferred channels

Source of high-temperature chemical kinetics data

measured and calculated chemical kinetic data → journal publications

data compilation → books. data bases.
e.g. **NIST database**
www.nist.gov

data evaluation → review articles

reevaluation and comparison of several articles → evaluated/recommended data

NIST Chemical Kinetics Database

www.nist.gov

⇒ Databases ⇒ Chemical Kinetics

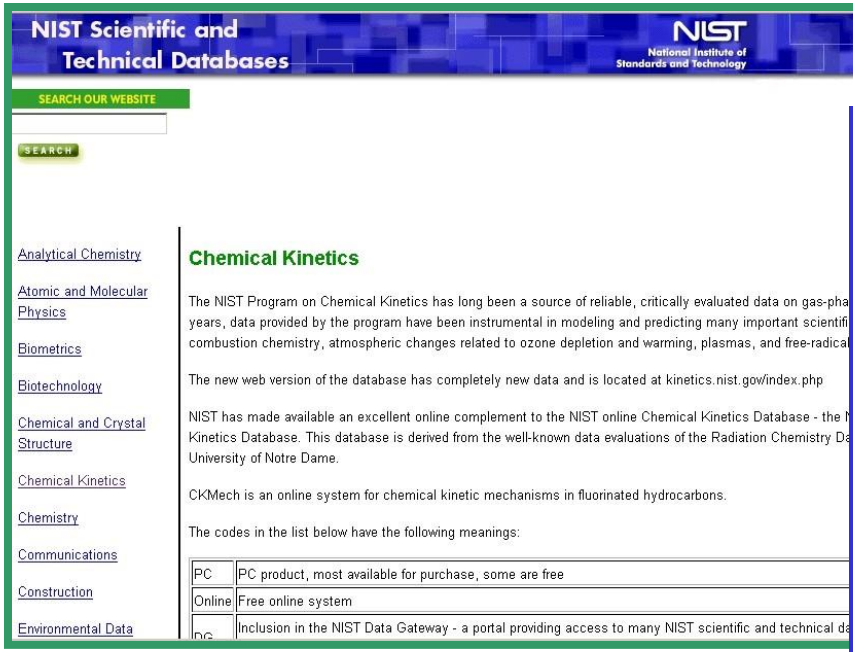
⇒ NIST Chemical Kinetics Online (http://kinetics.nist.gov/kinetics/)

NIST Chemical Kinetics Database

11.700 gas phase reactions

38.000 data entry

12.000 referenced articles



Chemical Kinetics

The NIST Program on Chemical Kinetics has long been a source of reliable, critically evaluated data on gas-pha years, data provided by the program have been instrumental in modeling and predicting many important scientifi combustion chemistry, atmospheric changes related to ozone depletion and warming, plasmas, and free-radical

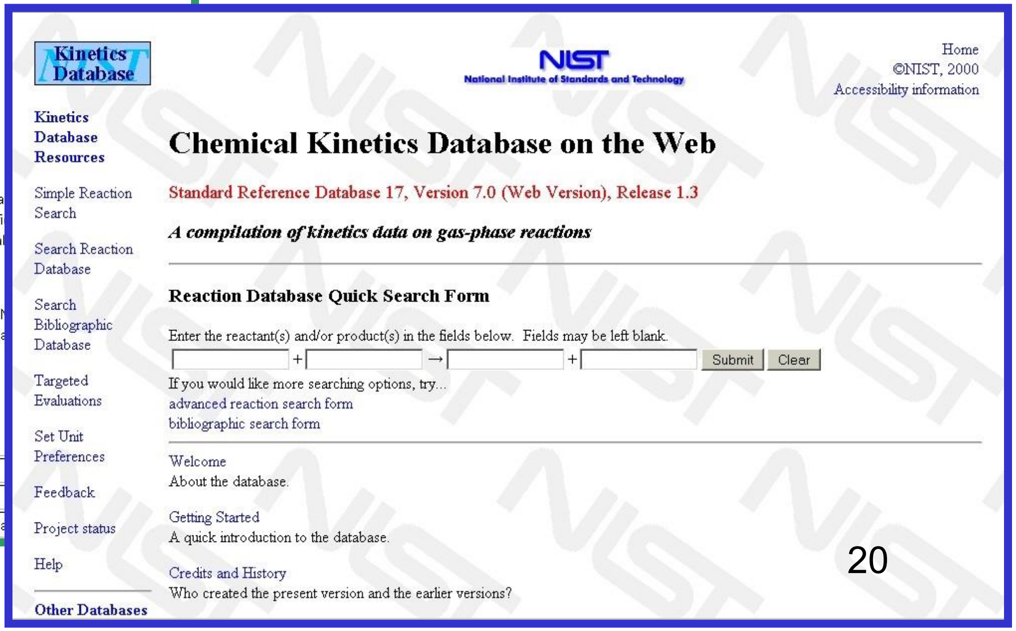
The new web version of the database has completely new data and is located at kinetics.nist.gov/index.php

NIST has made available an excellent online complement to the NIST online Chemical Kinetics Database - the N Kinetics Database. This database is derived from the well-known data evaluations of the Radiation Chemistry Da University of Notre Dame.

CKMech is an online system for chemical kinetic mechanisms in fluorinated hydrocarbons.

The codes in the list below have the following meanings:

PC	PC product, most available for purchase, some are free
Online	Free online system
DG	Inclusion in the NIST Data Gateway - a portal providing access to many NIST scientific and technical da



Chemical Kinetics Database on the Web

Standard Reference Database 17, Version 7.0 (Web Version), Release 1.3

A compilation of kinetics data on gas-phase reactions

Reaction Database Quick Search Form

Enter the reactant(s) and/or product(s) in the fields below. Fields may be left blank.

☐ + ☐ → ☐ + ☐

If you would like more searching options, try...

advanced reaction search form

bibliographic search form

Welcome

About the database.

Getting Started

A quick introduction to the database.

Credits and History

Who created the present version and the earlier versions?

NIST Chemical Kinetics Database 2

Author(s): Gierczak. T.; Talukdar. R.K.; Herndon. S.C.; Vaghjiani. G.L. Ravishankara. A.R.
Title: Rate coefficients for the reactions of hydroxyl radicals with methane and deuterated methanes
Journal: J. Phys. Chem. A:
Volume: 101
Page(s): 3125 - 3134
Year: 1997
Reference type: Journal article
Squib: 1997GIE/TAL3125-3134

Reaction: $CH4 + \cdot OH \rightarrow \cdot CH3 + H2O$
Reaction order: 2
Temperature: 196 - 420 K
Pressure: 0.13 Bar
Rate expression: $1.76\text{x}10^{-13}$ $(\text{cm}^3/\text{molecule s})$ $(\text{T}/298\text{ K})^{2.82}$ $\text{e}^{-1.96\text{ (}\pm 0.02\text{ kcal/mole)/RT}}$
Bath gas: He
Data type: Absolute value measured directly
Excitation technique: Flash photolysis (laser or conventional)
Analytical technique: Laser induced fluorescence

Rate coefficient uncertainties

Uncertainty factor f_j as defined in data evaluations

(Tsang, Warnatz, Baulch, Konnov):

uncertainty factor u_j

$$u_j = \frac{k_j^0}{k_j^{\min}} = \frac{k_j^{\max}}{k_j^0}$$

uncertainty parameter f_j

$$f_j = \log_{10}\left(u_j\right)$$

k_j^0 recommended value of the rate coefficient of reaction *j*

$k_j^{\min}$ possible minimal value of k_j

$k_j^{\max}$ possible maximal value of k_j

$\Rightarrow \quad [k_j^{\min}, k_j^{\max}]$ is the physically realistic range for the rate coefficients

assume that ln $k^{\min}$ and ln $k^{\max}$ deviate 3σ from ln k^0

$$\Rightarrow \quad \sigma^2(\ln k_j) = ((f_j \ln 10)/3)^2$$

1σ uncertainty limit (assuming that *u* corresponds to 3σ): $l = 10^{f/3}$

Uncertainty of *k* at a given temperature

Uncertainty of (direct) rate coefficient measurements:

very high quality data	uncertainty factor u= 1.26	⇔ f=0.1	⇔ ± 8 % (1σ)
typical good data	uncertainty factor u= 2.00	⇔ f=0.3	⇔ ±26 % (1σ)
typical data	uncertainty factor u= 3.16	⇔ f=0.5	⇔ ±47 % (1σ)

(high level) theoretical determinations:

TST/master equation calculations

best systems	uncertainty factor u= 2.00	⇔ f=0.3	⇔ ±26 % (1σ)
multi well, main channels	uncertainty factor u= 3.16	⇔ f=0.5	⇔ ±47 % (1σ)
multi well, minor channels	uncertainty factor u=10	⇔ f=1.0	

C. F. Goldsmith, A. S. Tomlin, S. J. Klippenstein: Uncertainty propagation in the derivation of phenomenological rate coefficients from theory: A case study of *n*-propyl radical oxidation
Proc. Combust. Inst., **34**, 177-185 (2013)

J. Prager, H. N. Najm, J. Zádor: Uncertainty quantification in the *ab initio* rate-coefficient calculation for the $CH_3CH(OH)CH_3+OH \rightarrow CH_3C.(OH)CH_3+H_2O$ reaction, *Proc. Combust. Inst.*, **34**, 583-590 (2013)

Example: the uncertainty of methane flame simulation results

The investigated methane flames:

- one dimensional, adiabatic, freely propagating, laminar, premixed stationary flame investigated at equivalence ratios φ = 0.70 (lean), 1.00 (stoichiometric), and 1.20 (rich)
- cold boundary conditions p = 1.0 atm and T = 298.15 K

Monitored outputs:

- laminar flame velocity
- maximum temperature
- maximum species concentration of H, O, OH, CH, CH_2

Uncertainty analysis of a laminar methane flame

Leeds Methane Oxidation Mechanism:
37 species and 175 reversible reactions
stationary, laminar 1D simulations

37 species: the recommended values of the enthalpies of formation and their variance was calculated from thermodynamic databases

175 reactions: uncertainty parameteres *f* were collected from Baulch *et al.*

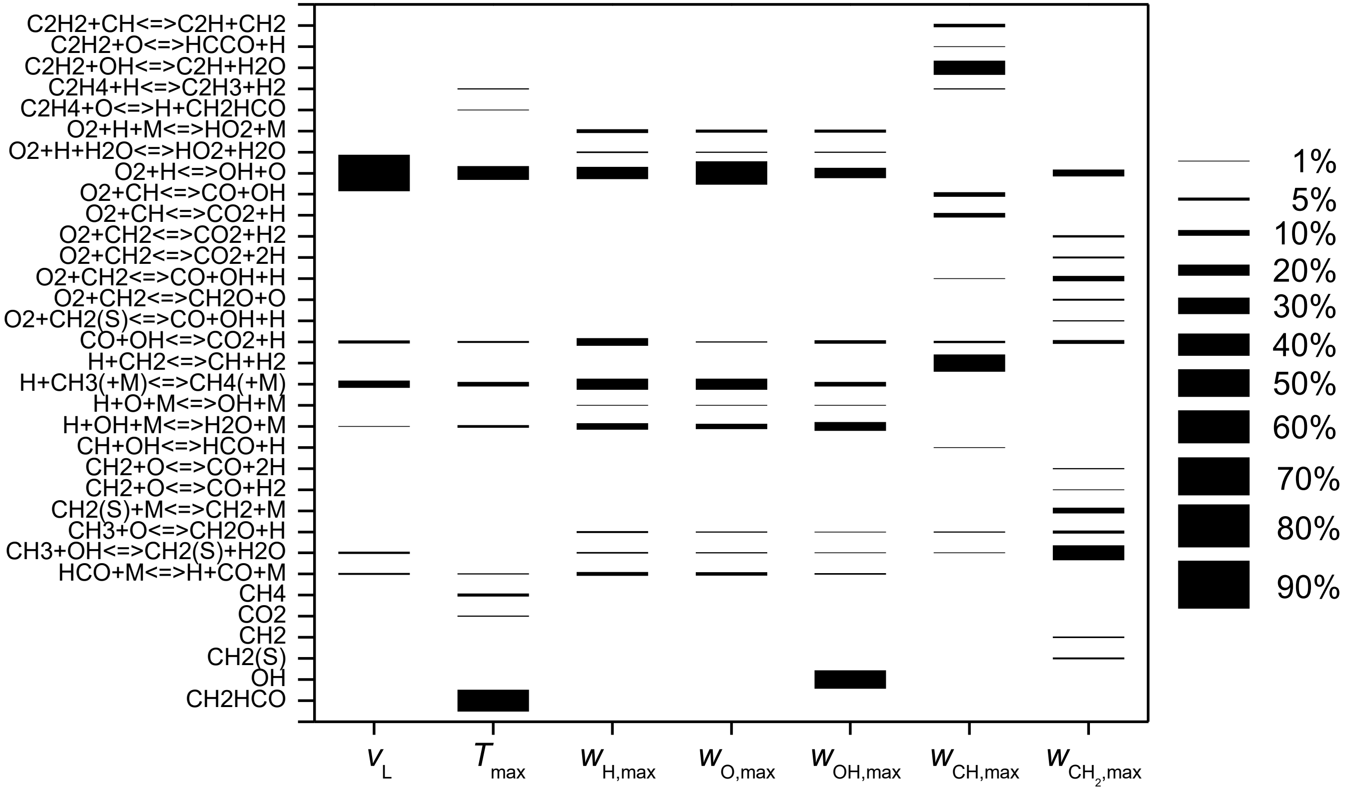
The investigated simulation results:
maximal flame temperature, laminar flame velocity,
maximal concentrations of radicals H, O, OH, CH, CH_2

Uncertainty analysis methods:
local uncertainty analysis, Morris' method,
Monte Carlo method, sensitivity indices

J. Zádor, I. Gy. Zsély, T. Turányi, M. Ratto, S. Tarantola, A. Saltelli: Local and global uncertainty analyses of a methane flame model, *J. Phys. Chem. A*, **109**, 9795-9807 (2005)

Local uncertainty analysis results

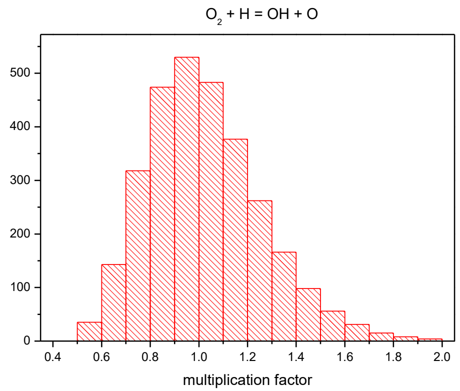
% contribution of parameter uncertainties to the uncertainty of the simulated results



$\varphi = 1.0$

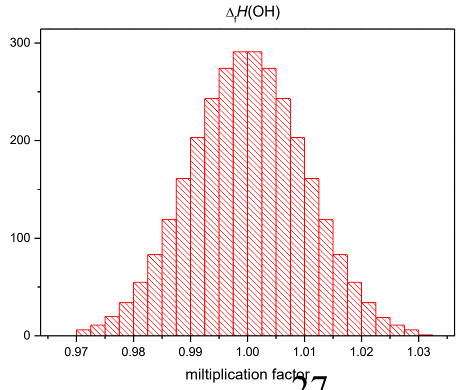
Assumed probability density functions of kinetic and thermodynamic parameters

The Monte Carlo and the sensitivity index methods require an assumption on the probability density functions (*pdf*s) of parameters



Rate coefficients:

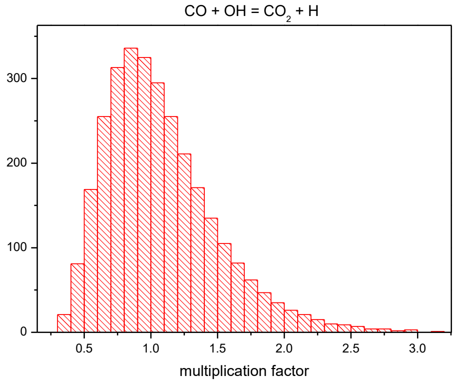
- log-normal distribution
- σ_j was calculated from the f_j uncertainty factor
- the log-normal distribution is clipped at $\pm 3\sigma$ (ln k_j)

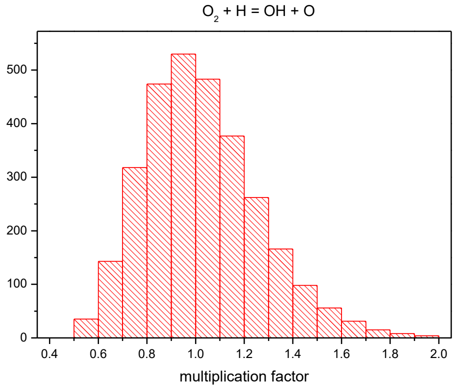


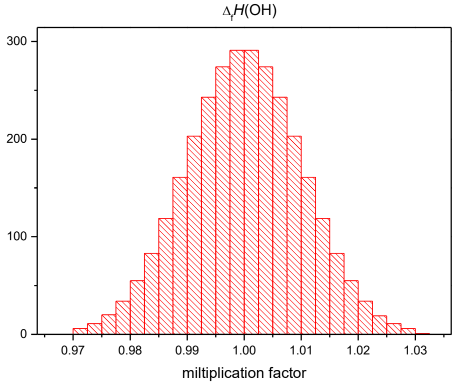
Enthalpies of formation:

- normal distribution
- σ is assessed on the basis of thermodynamic tables
- the normal distribution is clipped at $\pm 3\sigma$

pdf of parameters

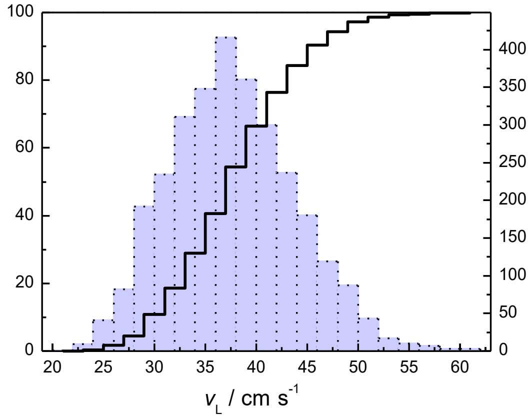


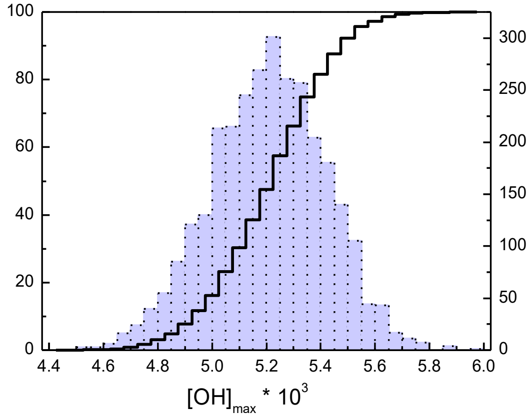


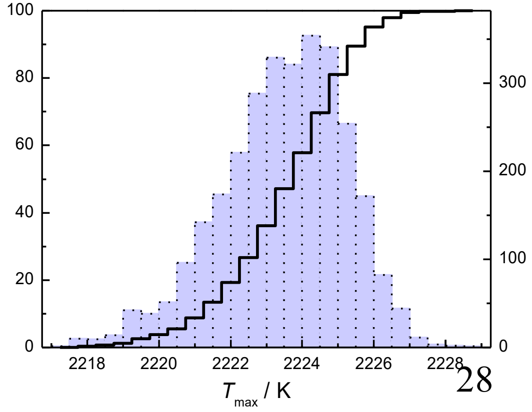


3,000 Monte Carlo simulations

pdf of simulation results







Comparison of the results of local and global (Monte Carlo) uncertainty analyses for a stoichiometric, stationary, flat methane-air flame

	result	calculated variances from	
		local	Monte Carlo
		uncertainty analyses	
flame velocity	38.1 cm/s	4.6 cm/s	6.2 cm/s
max. T	2224.2 K	2.8 K	1.7 K
max. w_{H}	2.14×10^{-4}	14.7%	12.6%
max. w_{O}	1.74×10^{-3}	13.3%	10.4%
max. w_{OH}	5.27×10^{-3}	3.6%	4.0%
max. w_{CH}	8.07×10^{-7}	46.3%	49.2%
max. w_{CH2}	2.54×10^{-5}	23.8%	24.0%

Methane flame uncertainty analysis: general conclusions

Good agreement is observed between the calculated total variances obtained through the local uncertainty analysis and the Monte Carlo method.

Better simulation results can be achieved, if the rate coefficients of a few reactions and the enthalpies of formation of a few species are known better (= with smaller variance)
These represent a small fraction of the total number of species/reactions.

Significant rate coefficients:

$O_2 + H = OH + O$
$O_2 + H + M = HO_2 + M$
$CO + OH = CO_2 + H$
$H + CH_3 + M = CH_4 + M$
$CH_3 + OH = CH_2(S) + H_2O$
$C_2H_2 + OH = C_2H + H_2O$
$C_2H_2 + CH = C_2H + CH_2$
$H + CH_2 = CH + H_2$

Significant enthalpies of formation:

OH
$CH_2(S)$
CH_2
CH_2OH
CH_2CHO

Uncertainty analysis study of the laminar methane flame the points to be corrected

Which were the weak points of
the previously discussed uncertainty analysis study?

„uncertainty of the rate coefficient" = uncertainty of Arrhenius parameter *A*
was considered only
→ What is the uncertainty of each Arrhenius parameter?

The used uncertainty parameters *f* were based on the direct measurements
→ Considering also the indirect measurements decreases the uncertainty

At the development of detailed reaction mechanisms,
the direct and indirect experimental results are both considered;
the nominal parameter set contains correlations
that have to be taken into account.
→ Considering the parameter correlations is needed

Temperature dependence of uncertainty factor *f*

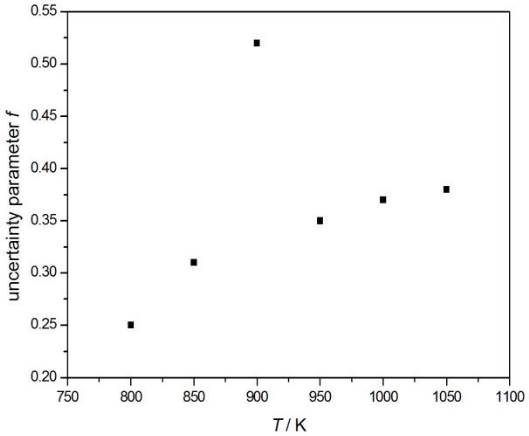
Uncertainty parameter *f* is either constant (Tsang, Warnatz, Konnov)

or defined in temperature regions (Baulch *et al.* evaluations):

$$f(T) = \begin{cases} f_1 & \text{if } T \in (T_1, T_2) \\ f_2 & \text{if } T = T_3 \\ \vdots & \vdots \end{cases}$$

f_1, f_2, f_3, … corresponds to the actual scatter of measurements in this temperature region.

We will call them f_{original} values.

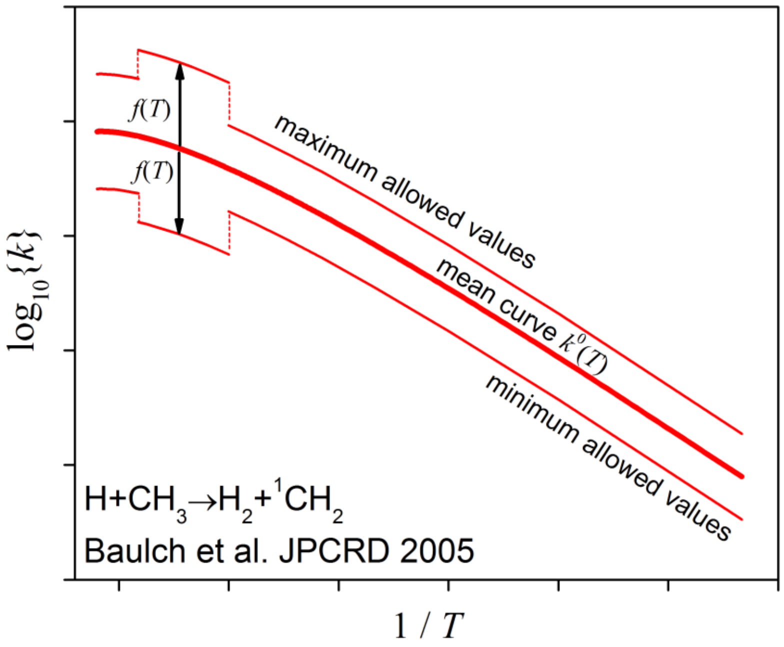


The temperature dependence of the rate coefficents imposes a relation among the uncertainty parameter *f* values at different temperatures.

The f_{original} values are not in accordance with the temperature dependence of the rate coefficient *k*

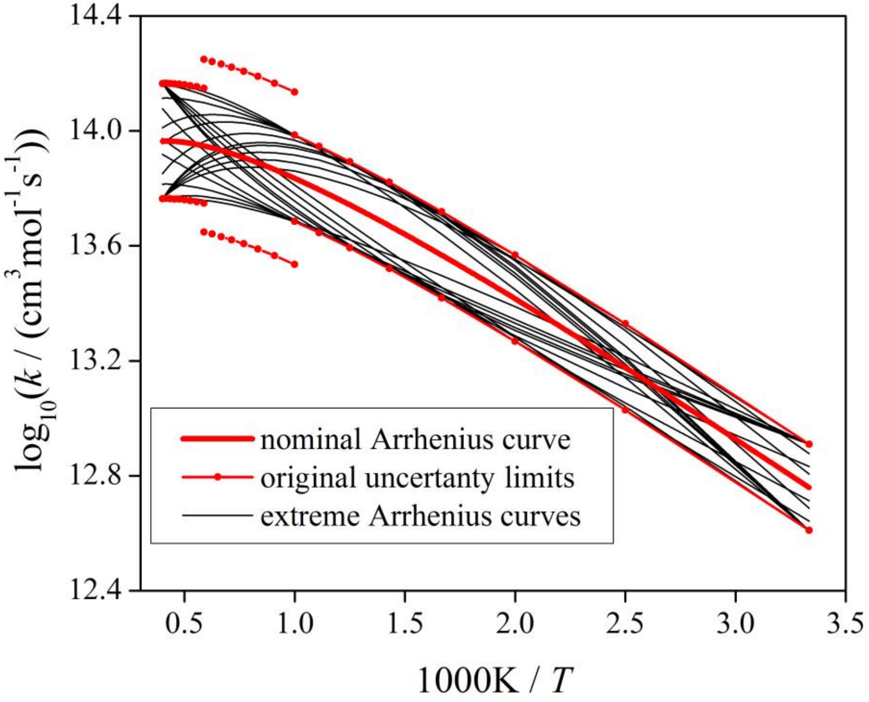
Getting consistent uncertainty factors *f*

Example from the
Baulch *et al.* (2005) evaluation:



Solution:

Drawing the possible extreme Arrhenius curves
span the realistic uncertainty limits
of the rate coefficient *k*:



The corrected *f* values are called $f_{extreme}$

Domain of uncertainty of Arrhenius parameters

The f_{extreme} (T) values define the uncertainty domain of the rate coefficient k in interval [T_1, T_2] with the temperature dependence of the rate coefficient k

The evaluations provide the uncertainty of k,
but the real parameters of the model are Arrhenius parameters A, n, E

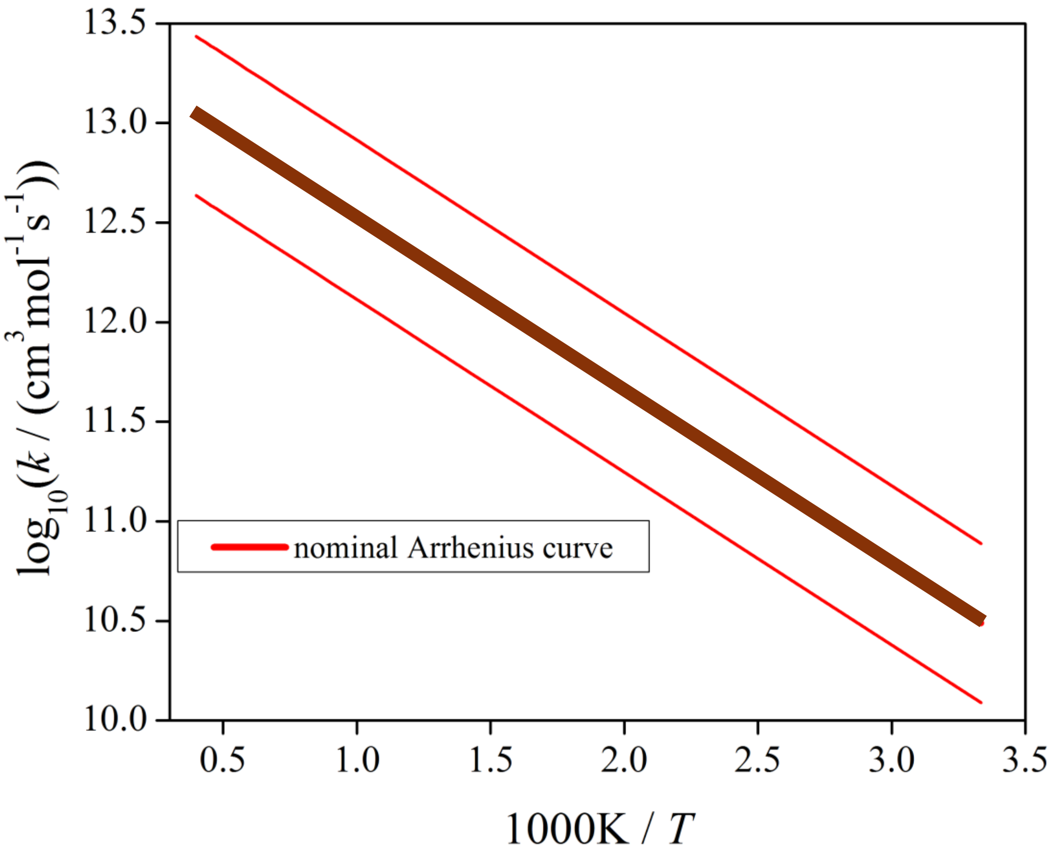
Better to deal with the transformed Arrhenius parameters ln A, n, E/R

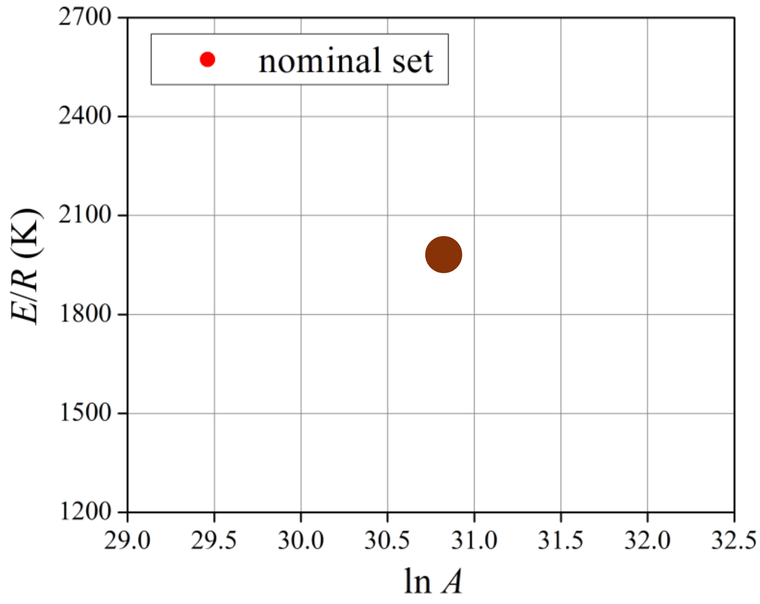
Statement: the extreme Arrhenius curves span the domain of uncertainty of the Arrhenius parameters.

Domain of uncertainty of Arrhenius parameters

The simplest case: temperature independent uncertainty of *k*

two Arrhenius parameters ln *A*, *E*/*R*

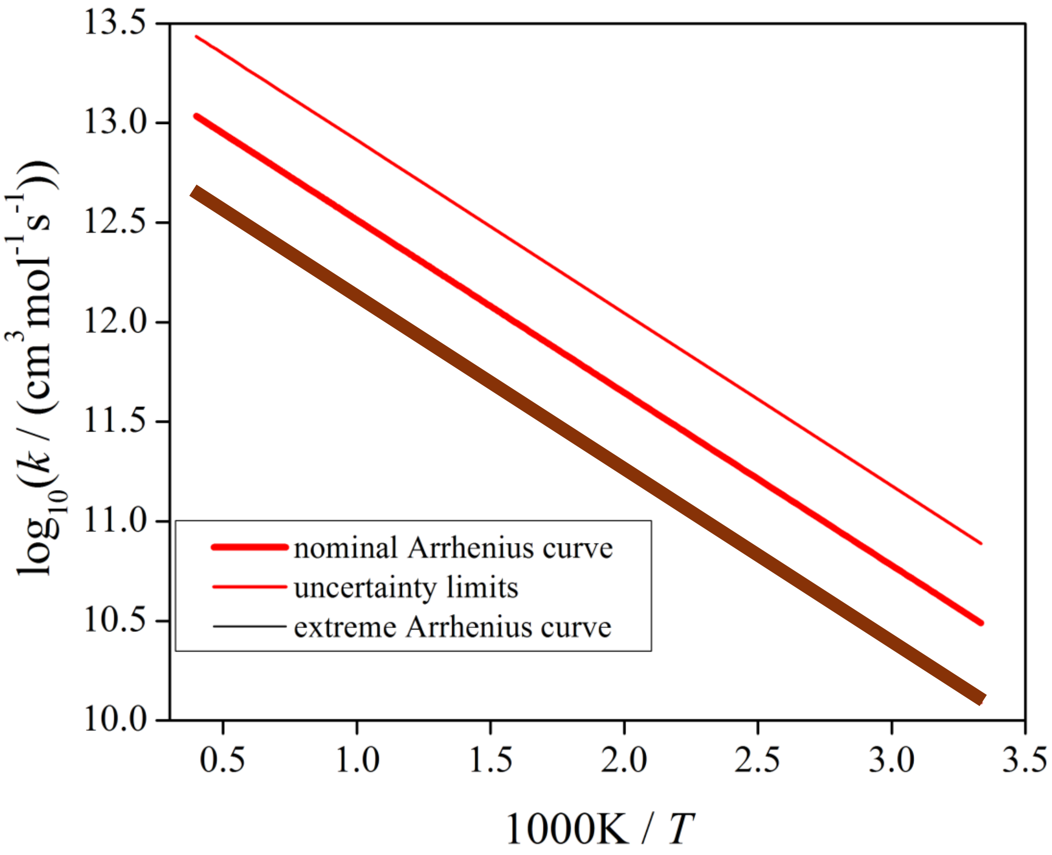


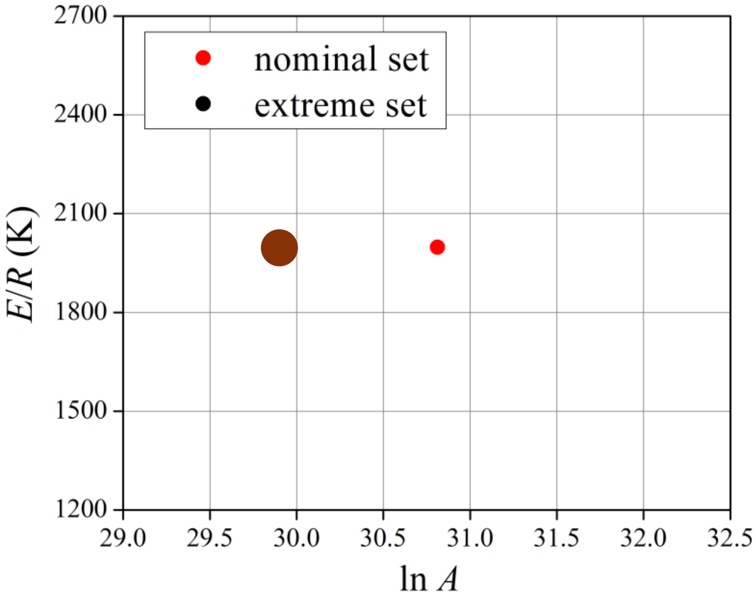


Domain of uncertainty of Arrhenius parameters

The simplest case: temperature independent uncertainty of *k*

two Arrhenius parameters ln *A*, *E*/*R*

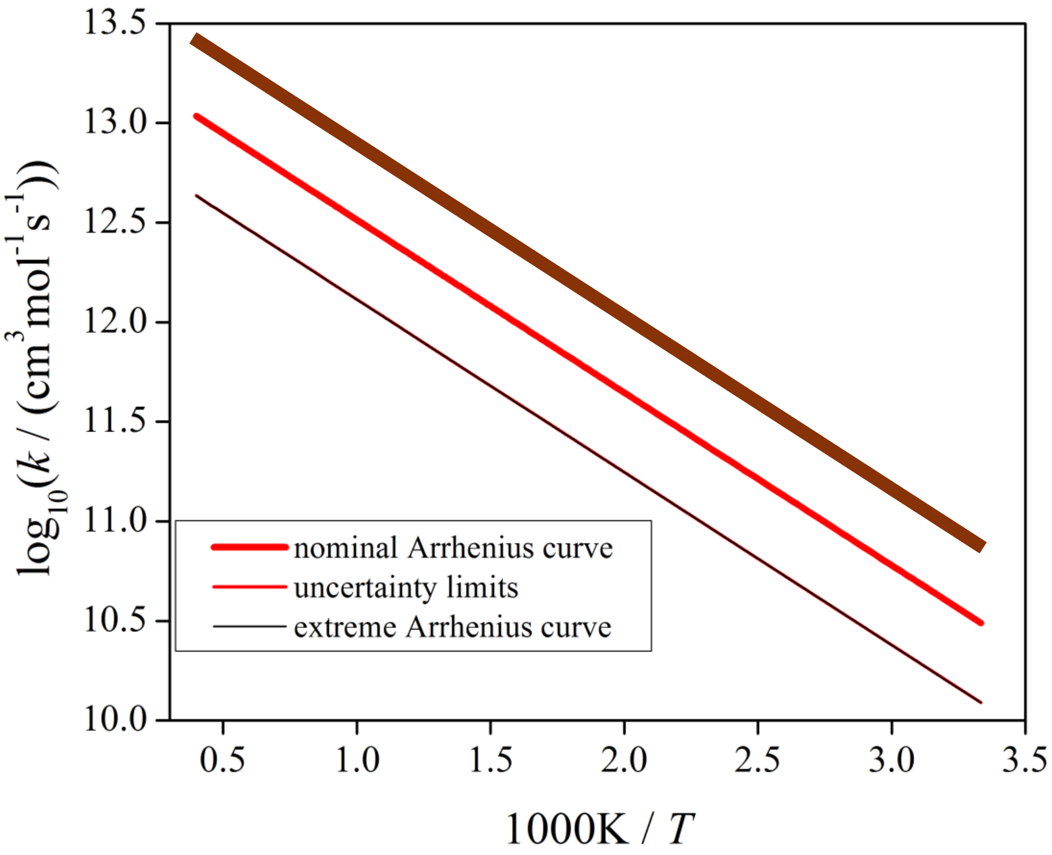


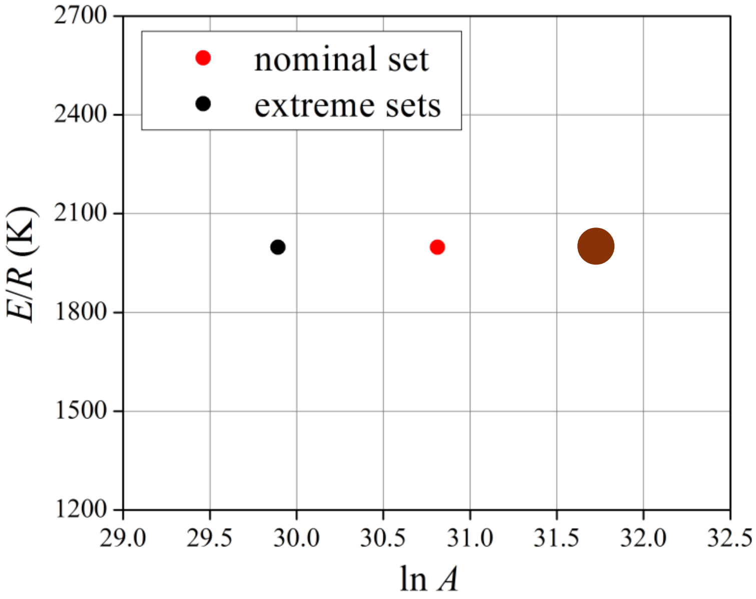


Domain of uncertainty of Arrhenius parameters

The simplest case: temperature independent uncertainty of *k*

two Arrhenius parameters ln *A*, *E*/*R*

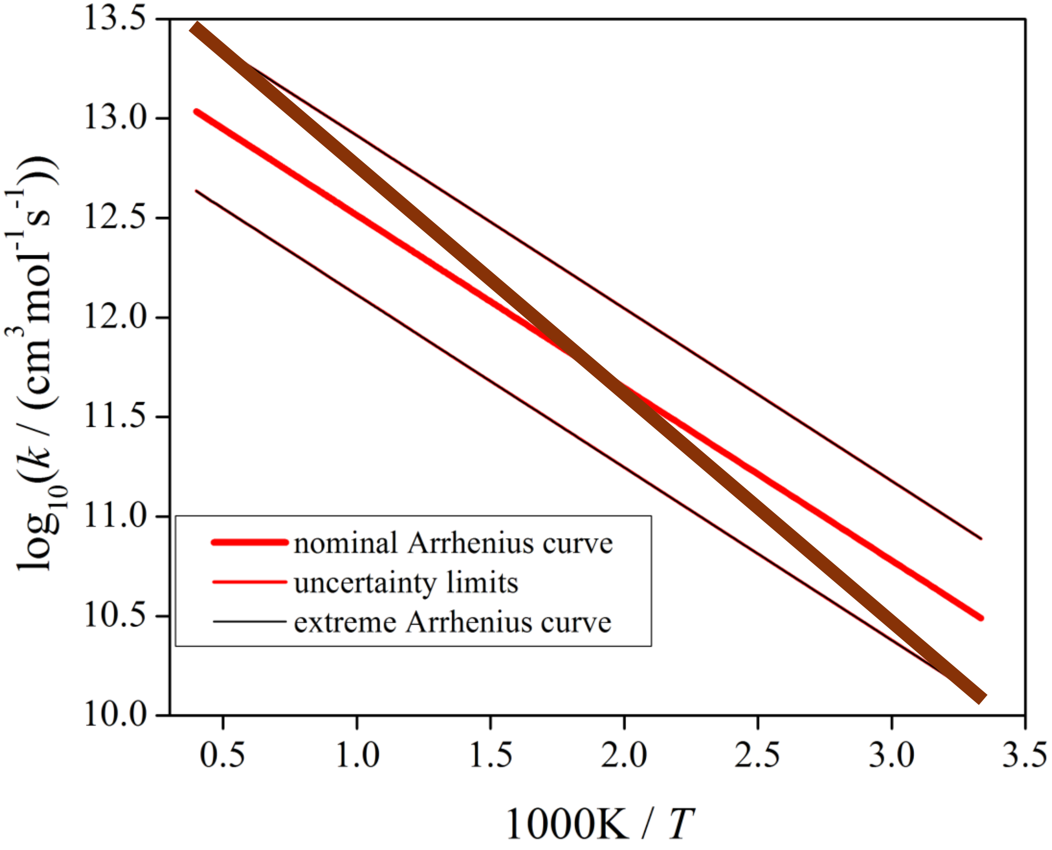


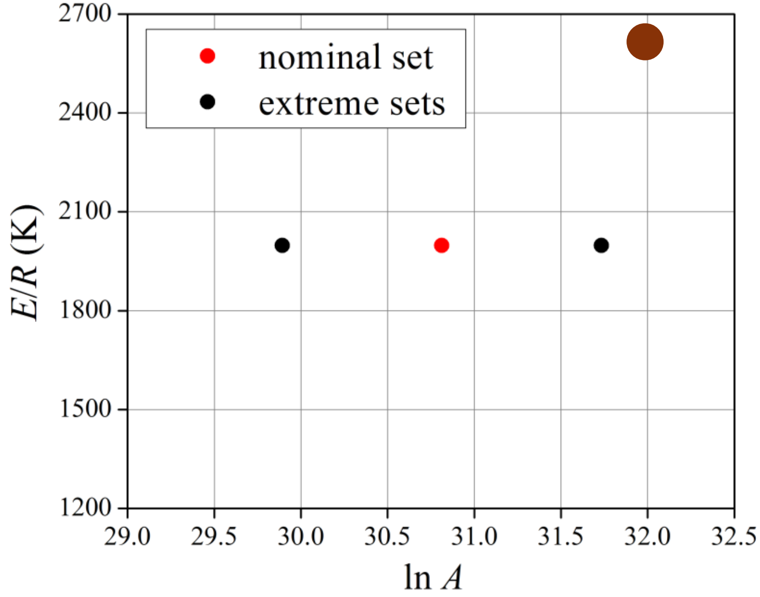


Domain of uncertainty of Arrhenius parameters

The simplest case: temperature independent uncertainty of *k*

two Arrhenius parameters ln *A*, *E*/*R*

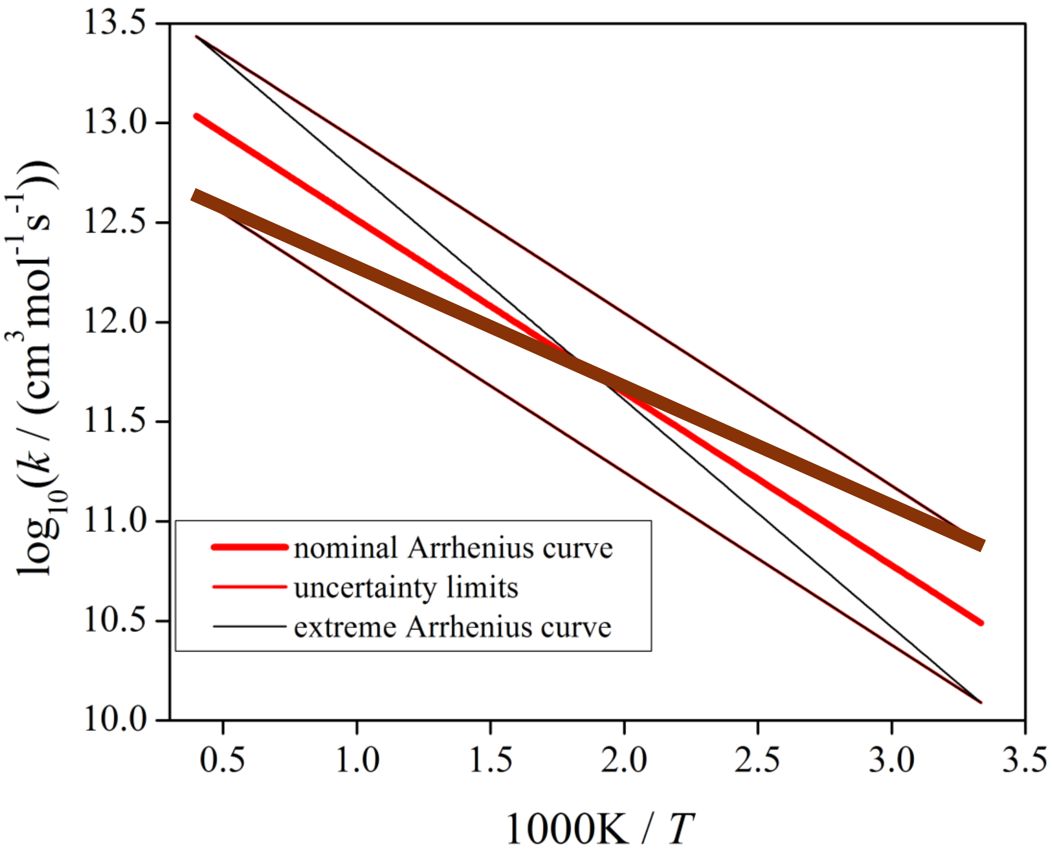


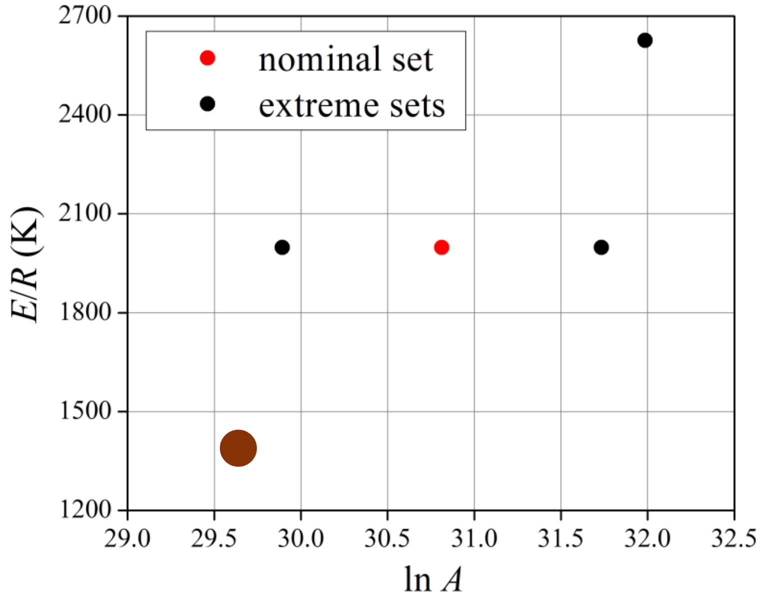


Domain of uncertainty of Arrhenius parameters

The simplest case: temperature independent uncertainty of *k*

two Arrhenius parameters ln *A*, *E*/*R*

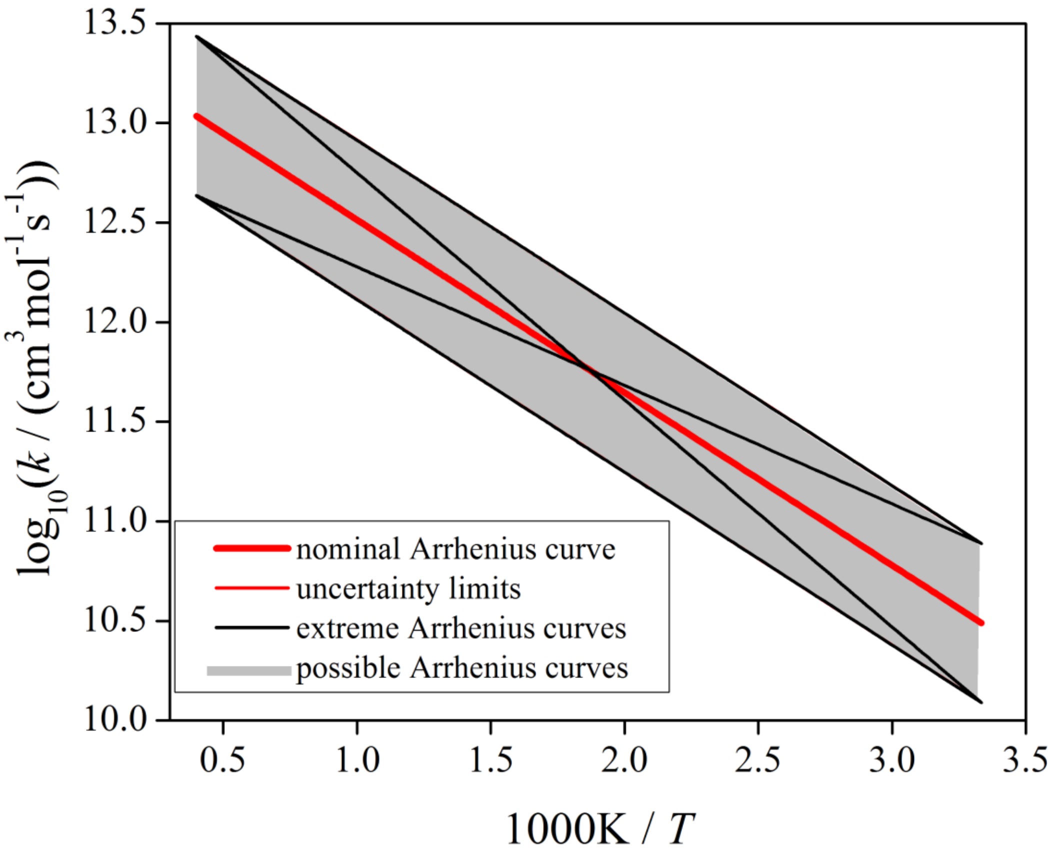


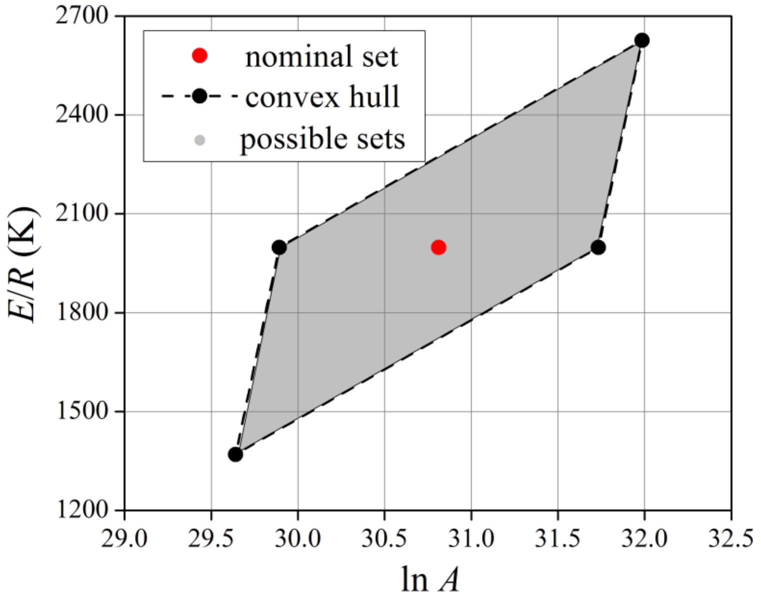


Domain of uncertainty of Arrhenius parameters

The simplest case: temperature independent uncertainty of *k*

two Arrhenius parameters ln *A*, *E*/*R*



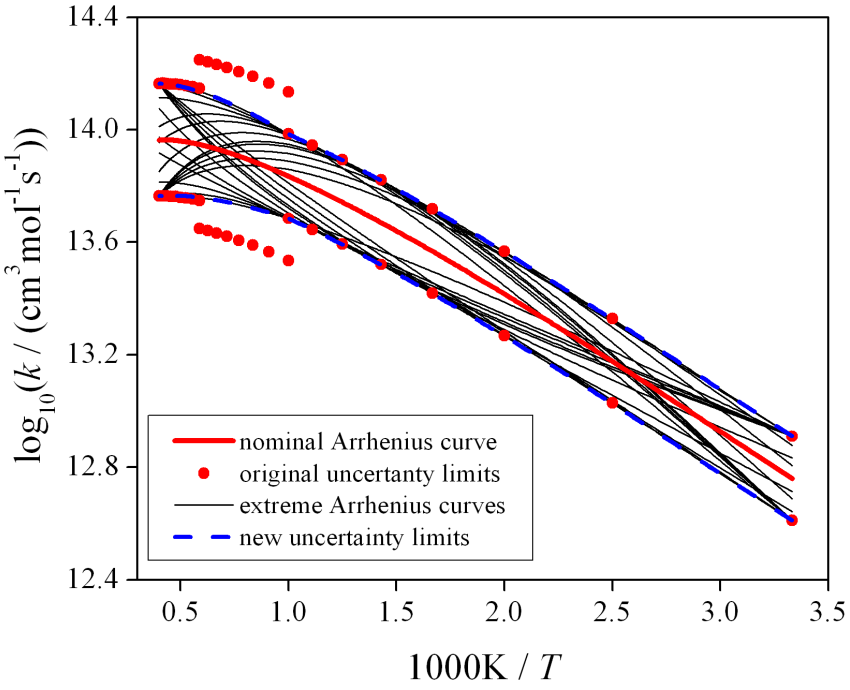


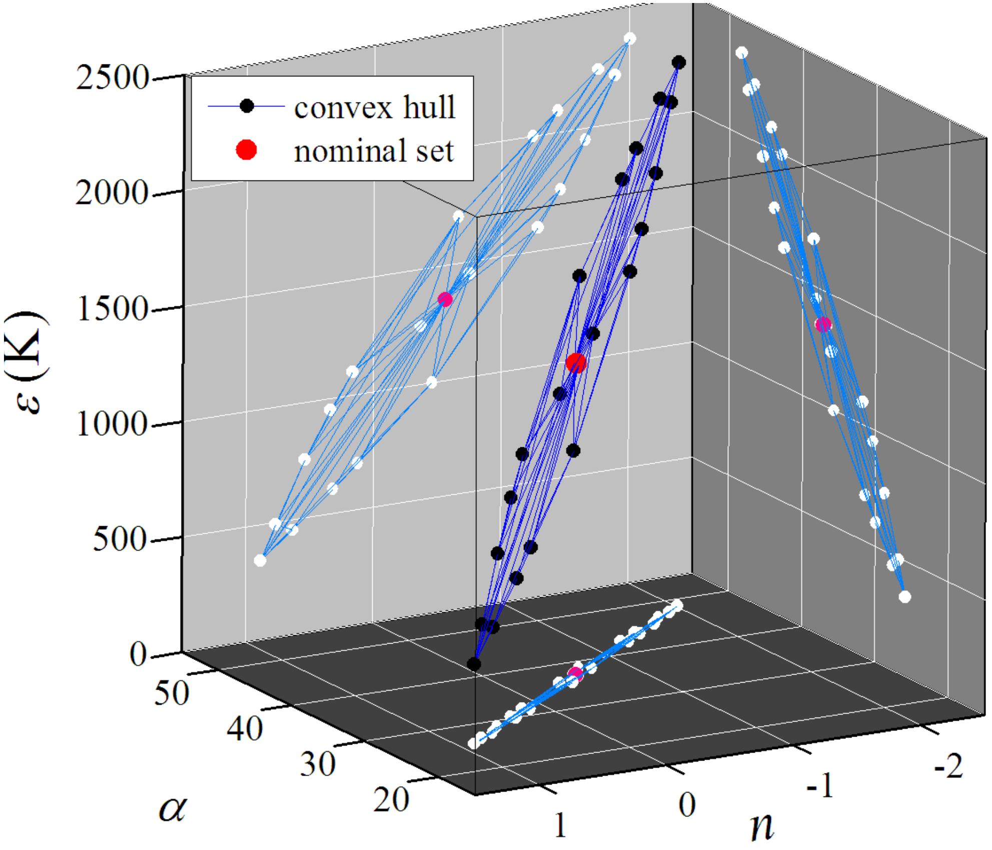
3D domain of Arrhenius parameters

The most complex case: temperature dependent uncertainty of *k*

three Arrhenius parameters α= ln *A*, *n*, ε= *E*/*R*

the extreme Arrhenius curves = vertices of the convex hull





Uncertainty parameter *f*

Definition of uncertainty factor *f*:

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

Calculation of the variance of ln *k* from uncertainty factor *f*:

(assuming 3σ deviation between $\log_{10} k^0$ and $\log_{10} k^{\max}$)

$$\sigma(\ln k)=\frac{\ln 10}{3}f$$

Instead of temperature dependent σ(ln *k*)

the covariance matrix of the Arrhenius parameters is needed!

extended Arrhenius expression:

$$\boxed{k(T)=AT^{n}\exp(-E/RT)}$$

linearized form:

$$\boxed{\underbrace{\ln\{k(T)\}}_{\kappa(\theta)}=\underbrace{\ln\{A\}}_{\alpha}+\underbrace{n}_{n}\cdot\ln\underbrace{\{T\}}_{\theta}-\underbrace{\{E/R\}}_{\varepsilon}\cdot\underbrace{\{T\}}_{\theta}{}^{-1}}$$

Relation between the σ of the rate coefficient and the covariance matrix of the Arrhenius parameters

Matrix-vector form of the linearized Arrhenius equation:

$$\boxed{\kappa(\theta) = \mathbf{p}^{\mathrm{T}}\boldsymbol{\theta}}$$

$$\boxed{\mathbf{p}^{\mathrm{T}} := [\alpha \;\; n \;\; \varepsilon]} \qquad \boxed{\boldsymbol{\theta}^{\mathrm{T}} := [1 \;\; \ln\theta \;\; -\theta^{-1}]}$$

The covariance matrix of the Arrhenius parameters and its relation to the uncertainty of the rate coefficient:

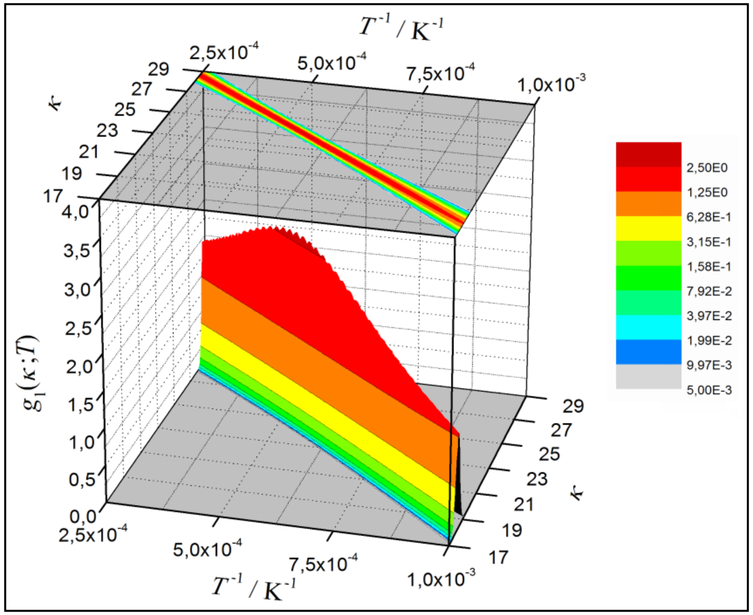
$$\boxed{\boldsymbol{\Sigma}_{\mathbf{p}} = \overline{(\mathbf{p}-\overline{\mathbf{p}})(\mathbf{p}-\overline{\mathbf{p}})^{\mathrm{T}}} = \begin{bmatrix} \sigma_{\alpha}^{2} & r_{\alpha n}\sigma_{\alpha}\sigma_{n} & r_{\alpha\varepsilon}\sigma_{\alpha}\sigma_{\varepsilon} \\ r_{\alpha n}\sigma_{\alpha}\sigma_{n} & \sigma_{n}^{2} & r_{n\varepsilon}\sigma_{n}\sigma_{\varepsilon} \\ r_{\alpha\varepsilon}\sigma_{\alpha}\sigma_{\varepsilon} & r_{n\varepsilon}\sigma_{n}\sigma_{\varepsilon} & \sigma_{\varepsilon}^{2} \end{bmatrix}}$$

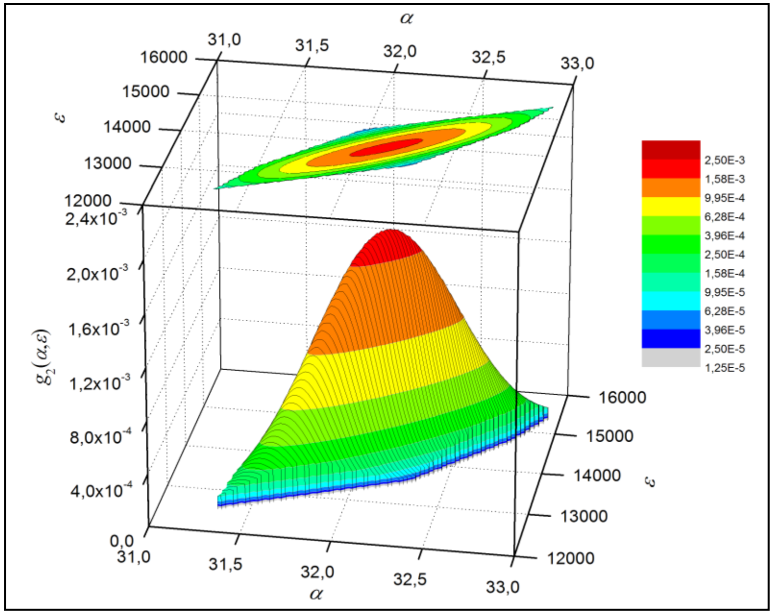
$$\boxed{\sigma_{\kappa}(\theta) = \sqrt{\boldsymbol{\theta}^{\mathrm{T}}\boldsymbol{\Sigma}_{\mathbf{p}}\boldsymbol{\theta}}}$$

⇒ the temperature dependent standard deviation of *k* can be calculated from a quadratic form.

Nagy, T.; Turányi, T. Uncertainty of Arrhenius parameters
Int. J. Chem. Kinet., **43**, 359-378 (2011)

Example: reaction O + $N_2O \rightarrow NO + NO$

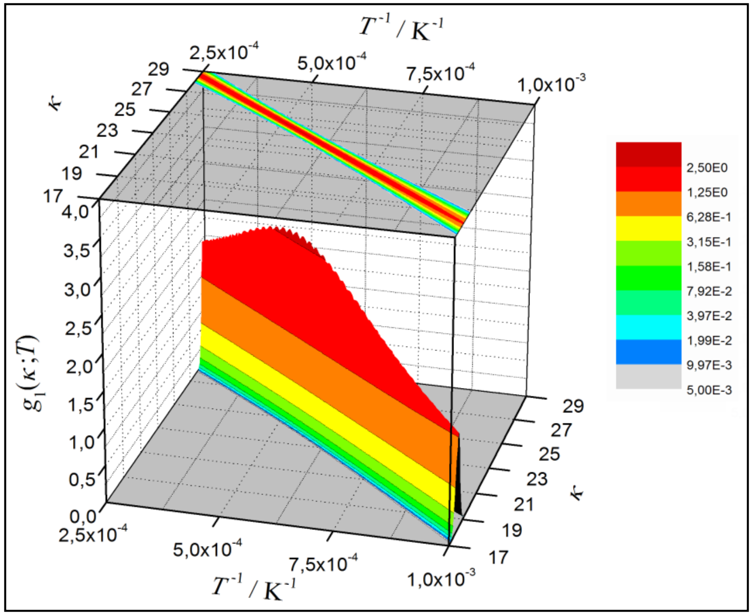


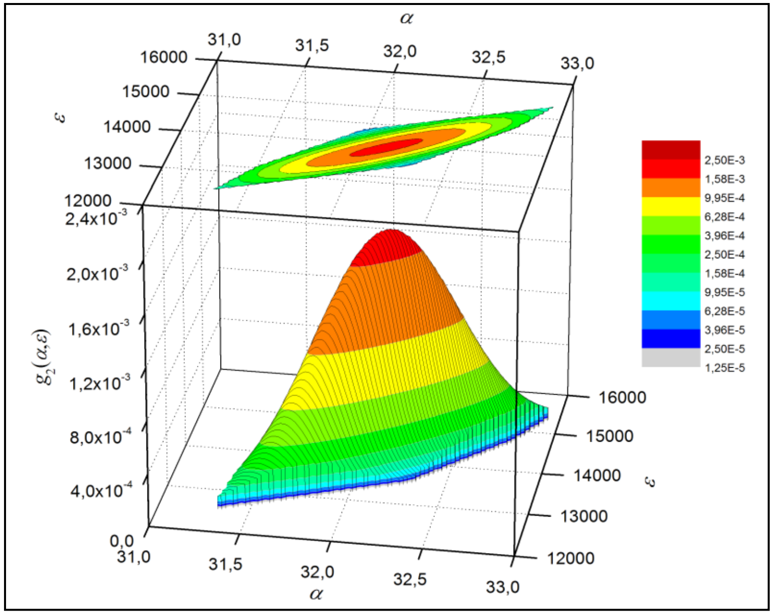


Temperature dependent
1D normal
probability density function (*pdf*)
of the rate coefficient
(1000 K – 4000 K)

Temperature independent
multivariate joint normal
probability density function (*pdf*)
of the Arrhenius parameters

Example: reaction O + $N_2O \rightarrow NO + NO$





Temperature dependent
1D normal
probability density function (*pdf*)
of the rate coefficient
(1000 K – 4000 K)

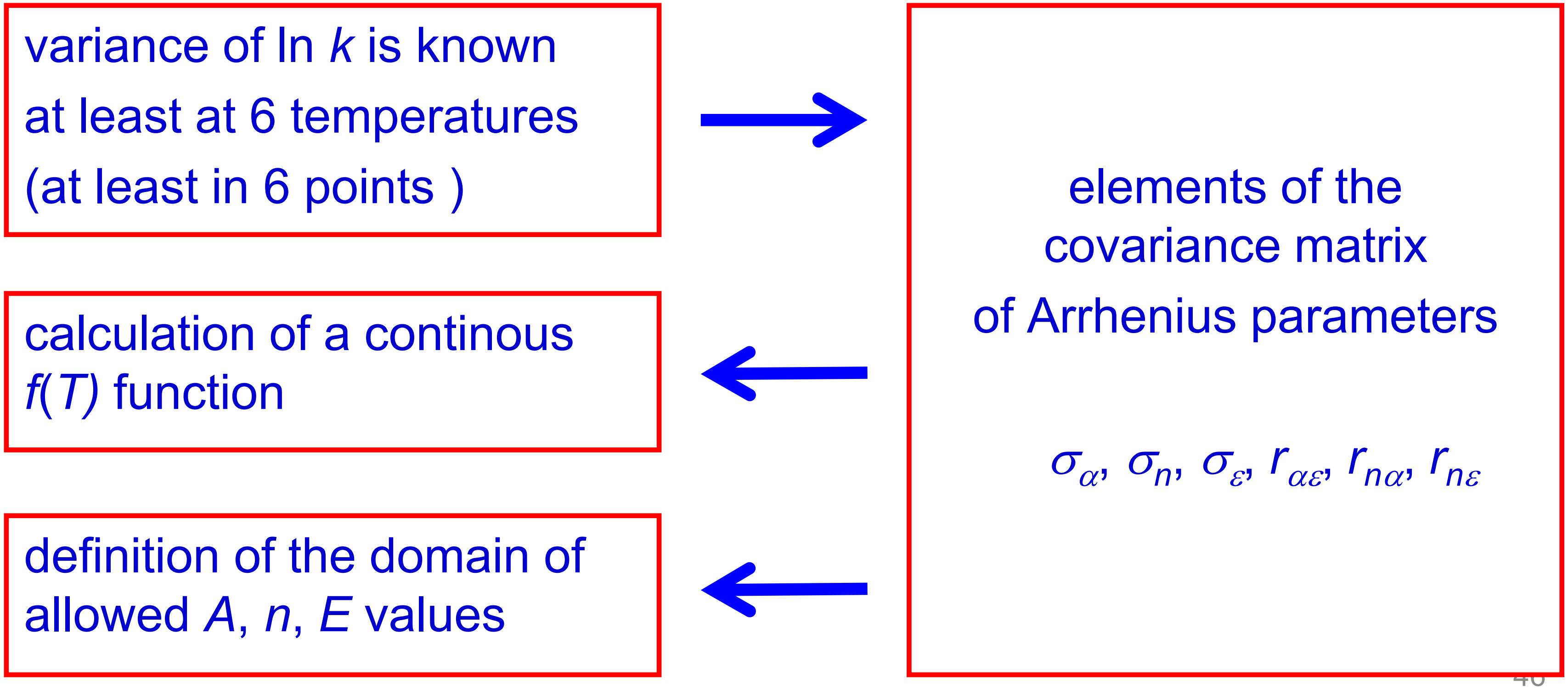
Temperature independent
multivariate joint normal
probability density function (*pdf*)
of the Arrhenius parameters

Calculation of the
covariance matrix of the Arrhenius parameters

$$\boxed{\sigma_\kappa(\theta)=\sqrt{\boldsymbol{\theta}^{\mathrm{T}}\boldsymbol{\Sigma}_{\mathbf{p}}\boldsymbol{\theta}}}$$

For the 3-parameter Arrhenius equation:

$$\boxed{\sigma_\kappa(\theta)=\sqrt{\sigma_\alpha^2+\sigma_n^2\ln^2\theta+\sigma_\varepsilon^2\theta^{-2}+2r_{\alpha n}\sigma_\alpha\sigma_n\ln\theta-2r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon\theta^{-1}-2r_{n\varepsilon}\sigma_n\sigma_\varepsilon\ln\theta\cdot\theta^{-1}}}$$



variance of ln *k* is known
at least at 6 temperatures
(at least in 6 points)

→

elements of the
covariance matrix
of Arrhenius parameters

σ_α, σ_n, σ_ε, $r_{\alpha\varepsilon}$, $r_{n\alpha}$, $r_{n\varepsilon}$

←

calculation of a continous
f(*T*) function

←

definition of the domain of
allowed *A*, *n*, *E* values

Features of the uncertainty parameter *f*

Baulch et al. (2005):

temperature independent *f* (constant *f*(*T*) function) about 50%

OR

a verbally defined f(T) function about 50%

”*f* = 0.1 at 800 K raising to 0.2 at 2000 K ”

Other sources:

NIST Chemical Kinetics Database, Tsang, Warnatz, Konnov

temperature independent *f* values.

Good features:

- *f* factors are available for several hundred reactions
- *f* factors are very realistic (to our experience)

Bad features:

- derivation of the *f* parameter is not documented
- temperature dependence is missing or not well defined

= cannot be used for the calculation of the uncertainty of the Arrhenius parameters

⇒ Reassessment of the uncertainty parameters is needed!

Reassessment of the *f*(*T*) functions is needed!

We have created an interactive website **https://k-evaluation.elte.hu/**
for the semiautomatic calculation of the *f*(*T*) functions.

Major steps for a given elementary reaction:

1 collection of all direct measurements and theoretical calculations
source: NIST Chemical Kientics Database + recent reviews

2 foreward direction: selected (direction with more data)
backward direction: converted to forward direction Arrhenius parameters

3 preparation of a datafile: each line one measurement/calculation
squib + temperature range + Arrhenius parameters

4 selection of a mean line (ln $k - 1/T$)
in the middle of uncertainty band is usually from Baulch *et al.*, 2005

5 Interactive website: interactive elimination of outliers

6 automatic calculation of „empirical" *f* points at several temperatures
fitting the elements of the covariance matrix to these points
plotting the experimental/theoretical results + the recalculated *f*(*T*)

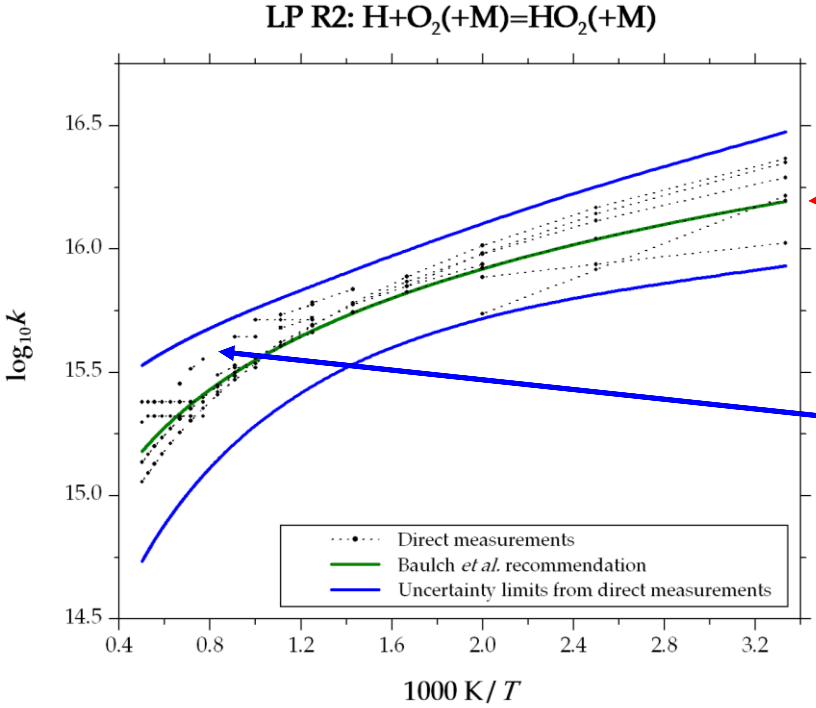
Example: reaction H + O_2 + M = HO_2 + M

We found about 60 experimental/theoretical rate expressions.

After the selection remained:

Ar bath gas: 9 experimentally determined and
1 theoretically calculated rate coefficient expressions
N_2 bath gas: 10 experimentally determined and
2 theoretically calculated rate coefficient expressions

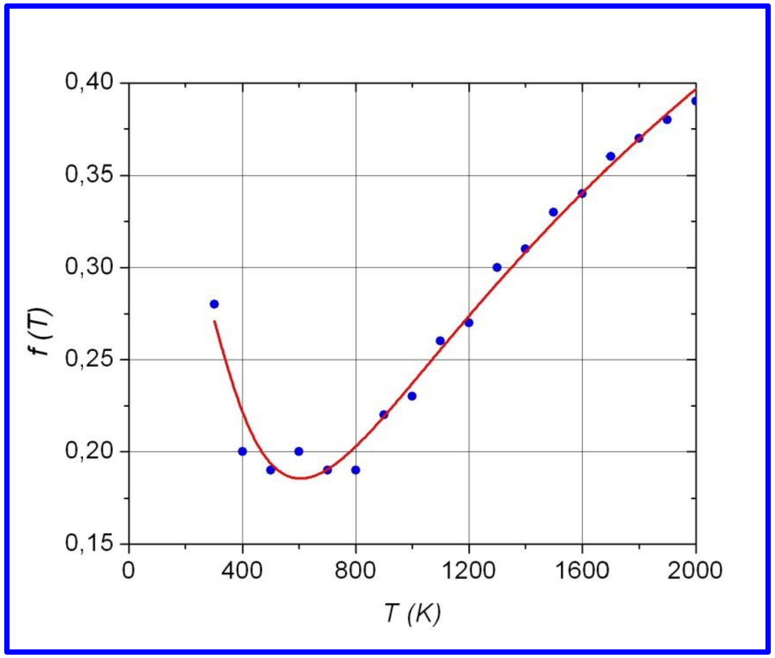
used together assuming *m*=0.5 (relative collision efficiency Ar to N_2)

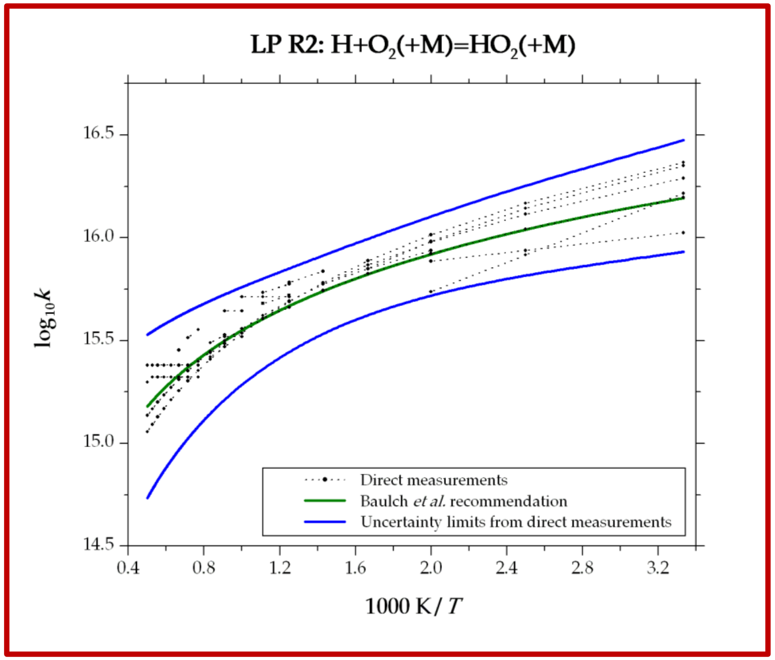


mean line:
Baulch *et al.*, 2005

rate expressions from
experiments and theory

Example: reaction $H + O_2 + M = HO_2 + M$



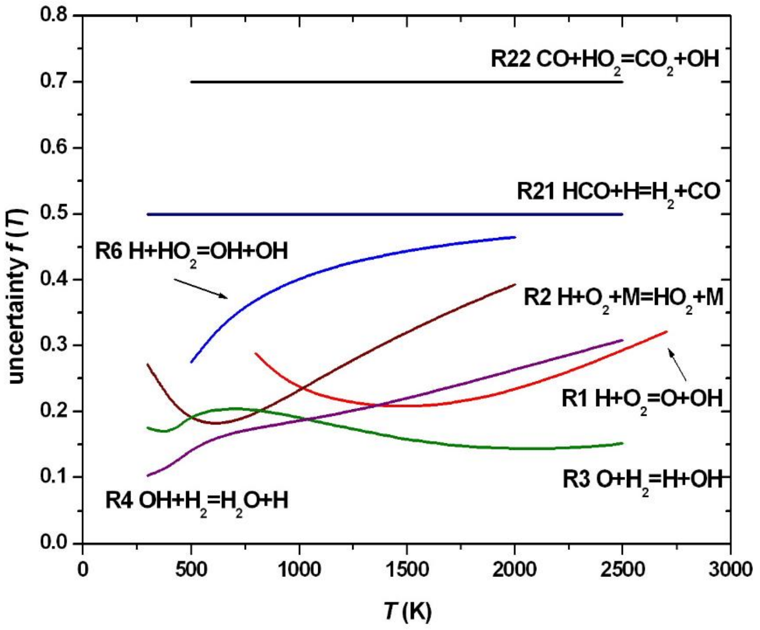


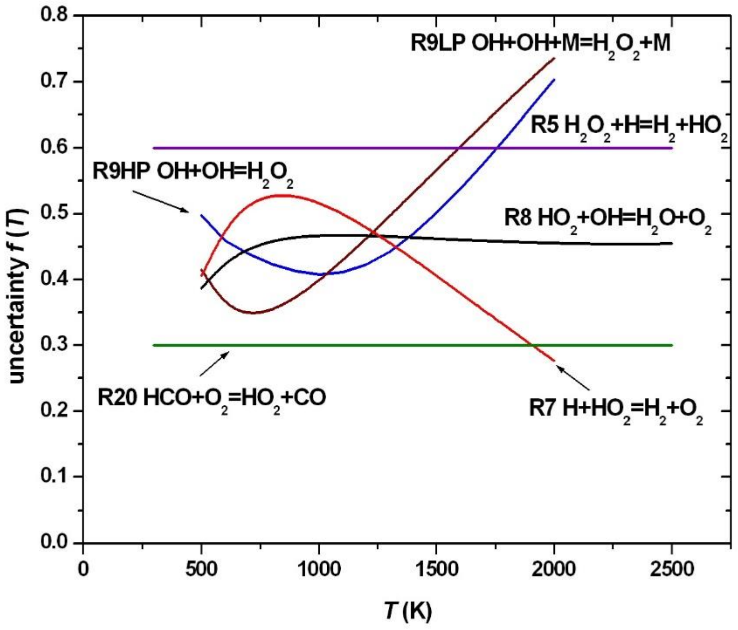
blue dots:
distance from the extreme experimental/theoretical values („empirical *f* points”)

red line:
calculated from the fitted elements of the covariance matrix
$\Rightarrow$ *a priori f*(*T*) function

blue line:
a priori
temperature dependent
k^{min} and k^{min} bounds
calculated from the
covariance matrix
of Arrhenius parameters

Evaluation of the *T*-dependent uncertainty of the rate coefficients is available for 208 reaction steps





T. Nagy, É. Valkó, I. Sedyó, I. Gy. Zsély, M. J. Pilling, T. Turányi: Uncertainty of the rate parameters of several important elementary reactions of the H_2 and syngas combustion systems, *Combust. Flame*, **162**, 2059-2076 (2015)

The *k-evaluation* website contains *f*(*T*) functions of 208 elementary reactions, stored as elements of the covariance matrix of Arrhenius parameters

Thank you for your attention!