COST CM1404 Training School on the analysis, uncertainty quantification, validation, optimization and reduction of detailed combustion mechanisms for practical use of smart energy carriers

Lecture 1-3
Uncertainty of data and parameters

Tamás Turányi

Chemical Kinetics Laboratory

Institute of Chemistry, Eötvös Loránd University (ELTE), Budapest. Hungary

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Rate coefficient uncertainties

Uncertainty factor f_j as defined in data evaluations

(Tsang, Warnatz, Baulch, Konnov):

uncertainty factor u_j uncertainty parameter f_j

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

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

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

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

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

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

1σ uncertainty limit (assuming that u corresponds to 3σ): $l = 10^{f/3}$ 2

Uncertainty of *k* at a given temperature

Uncertainty of (direct) rate coefficient measurements:

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

(high level) theoretical determinations:
TST/master equation calculations

best systems	uncertainty factor $u= 2.00 \Leftrightarrow f=0.3 \Leftrightarrow \pm 26 \%$ (1σ)
multi well, main channels	uncertainty factor $u= 3.16 \Leftrightarrow f=0.5 \Leftrightarrow \pm 47 \%$ (1σ)
multi well, minor channels	uncertainty factor $u=10.00 \Leftrightarrow f=1.0$

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)
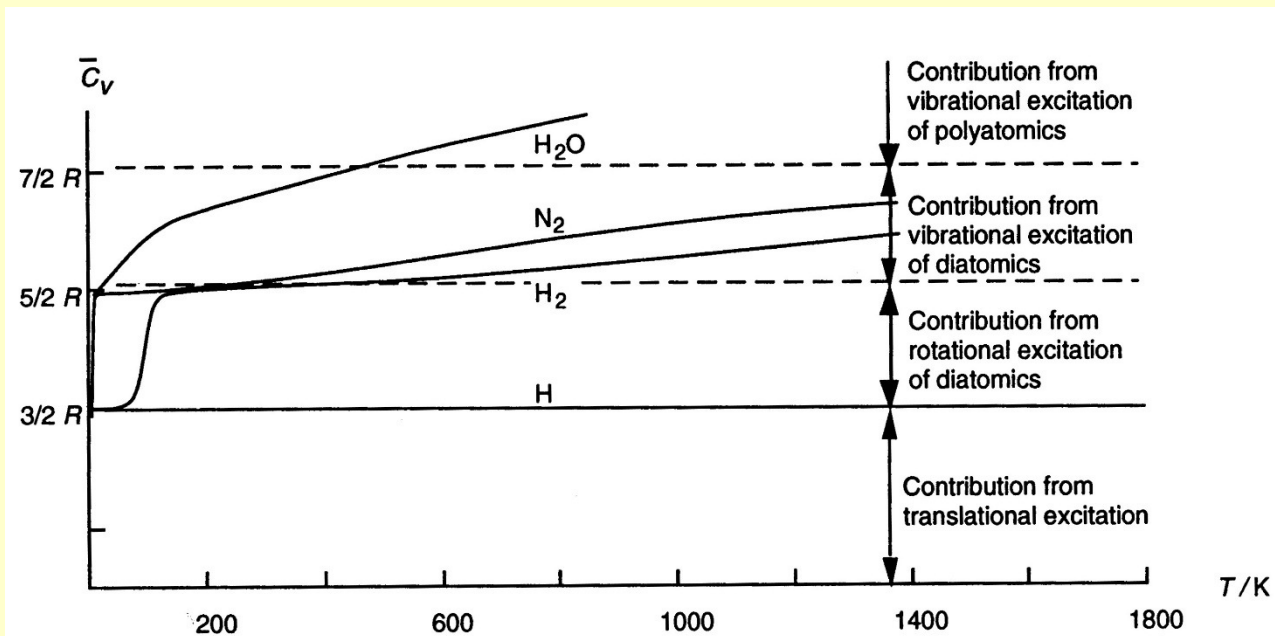
Temperature dependence of thermodynamic data

NASA polynomials

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

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

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

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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 thermodynamic data

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

ΔH_f - can be computed

   (for small molecules only; not so easy)
   - can be determined experimentally by
   • measuring the equilibrium constant of a reaction
      $\rightarrow$ reaction enthalpy $\rightarrow$ 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

Determination of the enthalpies of formation

Methods for the determination of enthalpies of formation ΔH_f :

1) direct experimental determination:
   calorimetry; synthesis from reference state elements
   $$H_2 + \tfrac{1}{2}\, O_2 = H_2O \quad \text{applicable for few compounds only}$$

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) generally applicable method:
   indirectly from experimentally measured reaction enthalpies $\Delta_r H^{\ominus}$
   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   http://atct.anl.gov/

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

using n direct experimental determination: $H_f^{\ominus}(j) = A_j$ $j = 1, \ldots ,n$

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

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

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

If the errors of the measurements are also taken into account
          $\Rightarrow$ **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 $\Delta_r H^0$ 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 calcaulation 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)

Using thermodynamic data in combustion simulations

ΔH_f $\Rightarrow$ calculation of heat production in a reacting mixture

       $\rightarrow$ calculation of temperature changes

       $\Rightarrow$ calculation of $\Delta_r G^0$

c_p $\Rightarrow$ calculation of temperature changes

ΔS $\Rightarrow$ calculation of $\Delta G = \Delta H - T\Delta S$

       $\rightarrow$ calculation of the equilibrium constant

       $\rightarrow$ calculation of the rate coefficient of reverse reactions

Uncertainty of thermodynamic data

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 $\Rightarrow$

$\Delta_r G = \Delta_r H - T \Delta_r S \Rightarrow \Delta_r G$ 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

Prior and posterior uncertainties of chemical kinetic data

direct an indirect measurements
uncertainty of the rate coefficients
mechanism optimisation
posterior uncertainties

Direct and indirect measurements

Direct measurements:
- determination of the rate coefficient of a single elementary reaction at a given temperature, pressure, and bath gas
- the rate coefficient values are published

Theoretical (direct) determinations:
- TST/master equation calculations
- the rate coefficients are published at given T, p
- parameterised T, p dependence of rate coefficient k

Indirect measurements:
- a property of the whole combustion system is measured
- interpretation is based on a detailed mechanism
- *e.g.* laminar flame velocities, ignition delays, concentration profiles

Direct and indirect measurements 2

direct measurement:

determination of the rate coefficient of a single elementary reaction
at a given temperature, pressure, and bath gas

the rate coefficients are published

very high quality data uncertainty (3σ) factor of 1.3 (f=0,1)

$\pm$10 % (1σ)

typical data uncertainty (3σ) factor of 3.0 (f=0,5) $\pm$44 % (1σ)

(high level) theoretical determinations:

TST/master equation calculations

typical uncertainty (3σ):   factor of 3   (f=0.5)   (main channels)

factor of 10   (f=1.0)   (minor channels)

see: Goldsmith *et al. PCI*, 2013; Prager *et al., PCI*, 2013

indirect measurements:

simulation with a detailed mechanism is needed for the interpretation

ignition delay times: good 1 σ uncertainty: 10%

flame velocities: good 1 σ uncertainty: 1 cm/s (hydrocarbon flames)

Uncertainty of reaction rate parameters

Reaction rate parameters:
Arrhenius parameters *A, n, E* ,
3rd body collision efficiencies,
(parameters of presure dependence: Lindemann and Troe parameters)
(enthalpies of formation)

prior **uncertainty of reaction rate parameters:**
    uncertainty of reaction rate parameters, deduced from
    available direct measurement data and theoretical calculations

posterior **uncertainty of reaction rate parameters:**
    uncertainty of reaction rate parameters, deduced from fitting to
    direct measurement data + theoretical calculations results +
    indirect measurement data

Determination of the *prior*

uncertainty of the reaction rate parameters

Getting good prior uncertainties

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

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

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

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

We will call them $f_{original}$ values.
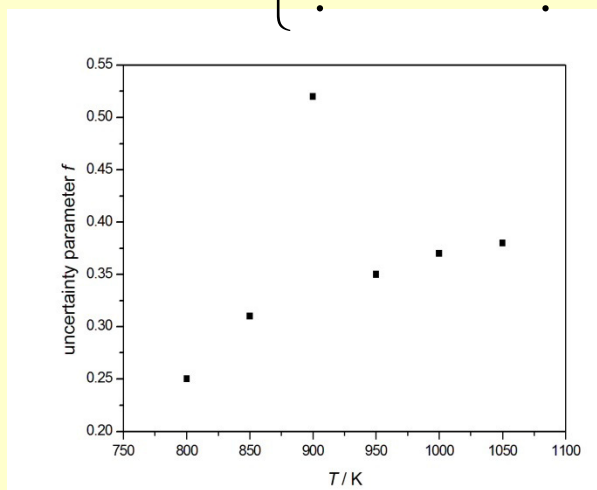
The temperature dependence of the rate coefficents imposes a relation among the uncertainty parameter f values at different temperatures.

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

Getting good prior uncertainties *f*

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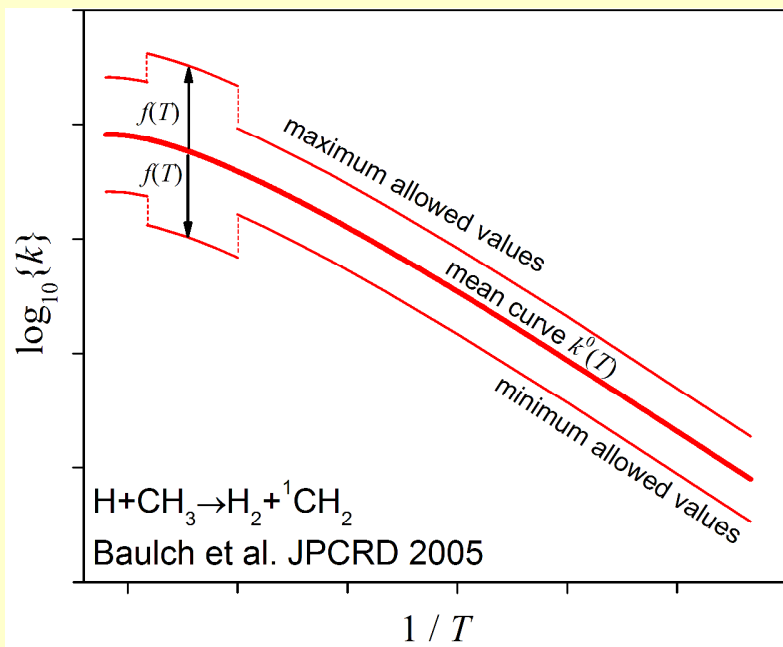
Solution:

Drawing the possible extreme Arrhenius curves
span the realistic uncertainty limits
of the rate coefficient *k*:
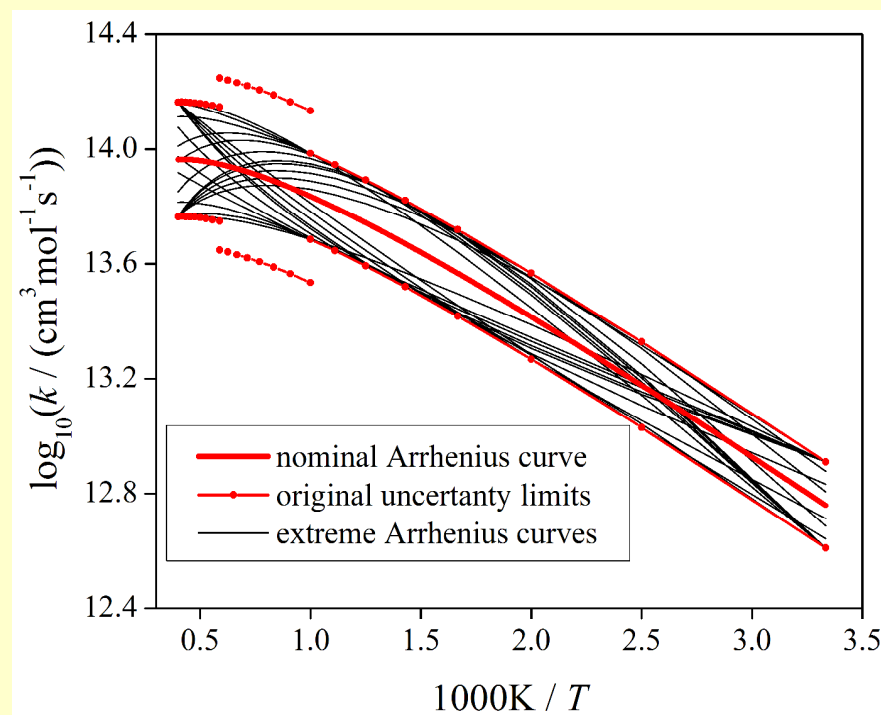
The corrected *f* values are called *f*$_{extreme}$

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

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two Arrhenius parameters   ln A, E/R

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Domain of uncertainty of Arrhenius parameters

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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
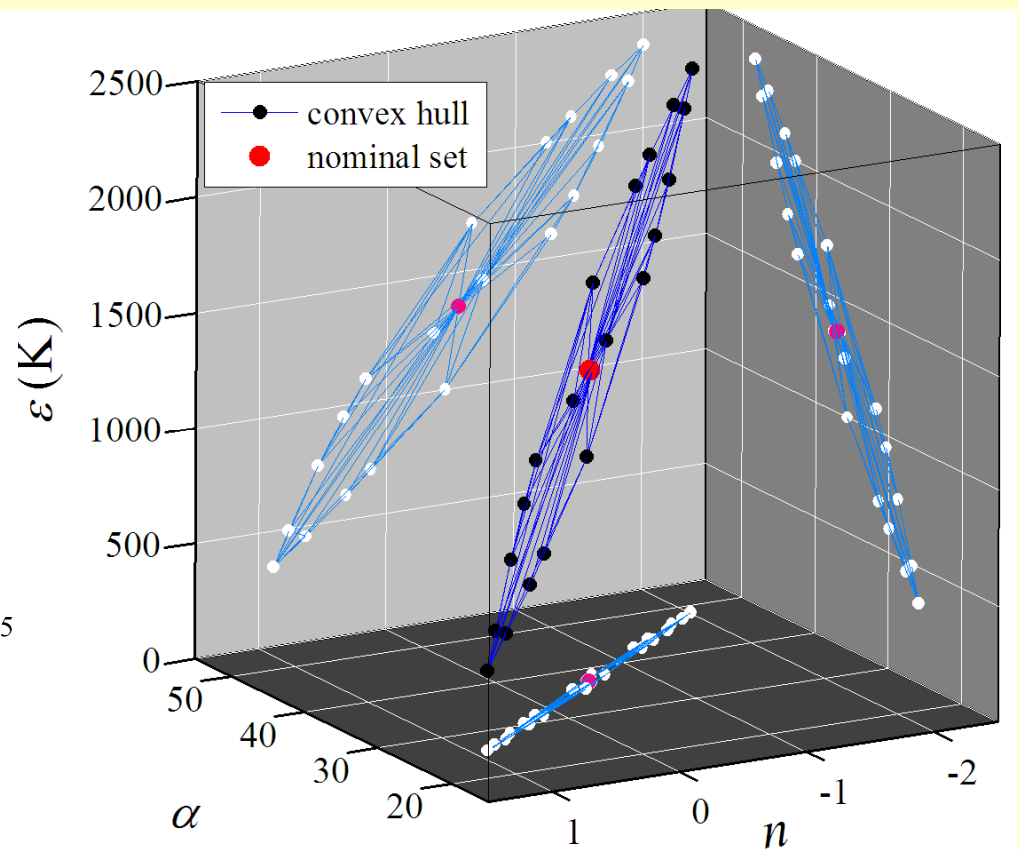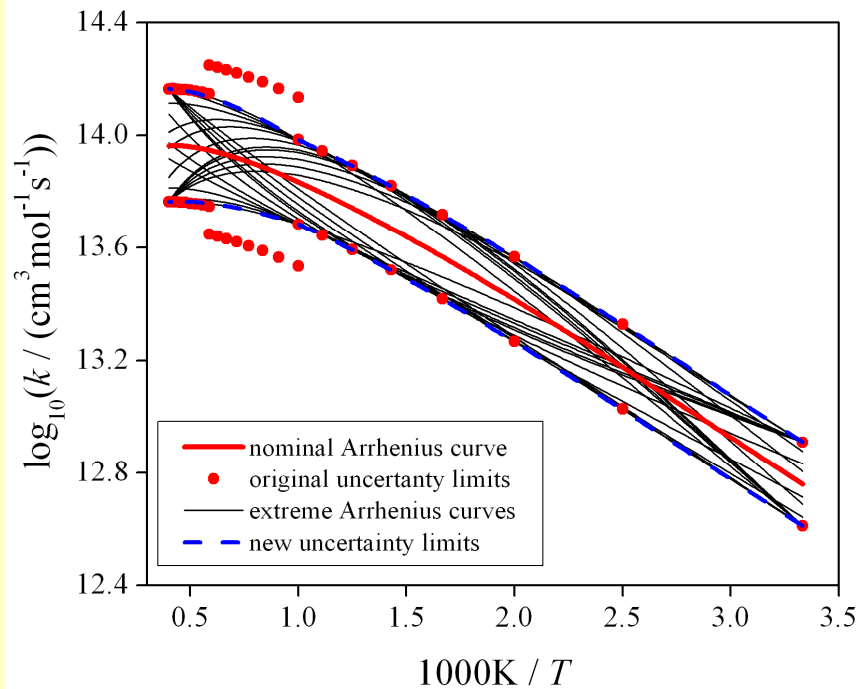
Uncertainty parameter f

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:

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

linearized form:

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

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

Matrix-vector form of the linearized Arrhenius equation:

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

$$\mathbf{p}^T := \begin{bmatrix} \alpha & n & \varepsilon \end{bmatrix}$$

$$\boldsymbol{\theta}^T := \begin{bmatrix} 1 & \ln\theta & -\theta^{-1} \end{bmatrix}$$

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

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

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

⇒ the temperature dependent standard deviation of *k* can be calculated from a quadratic form.
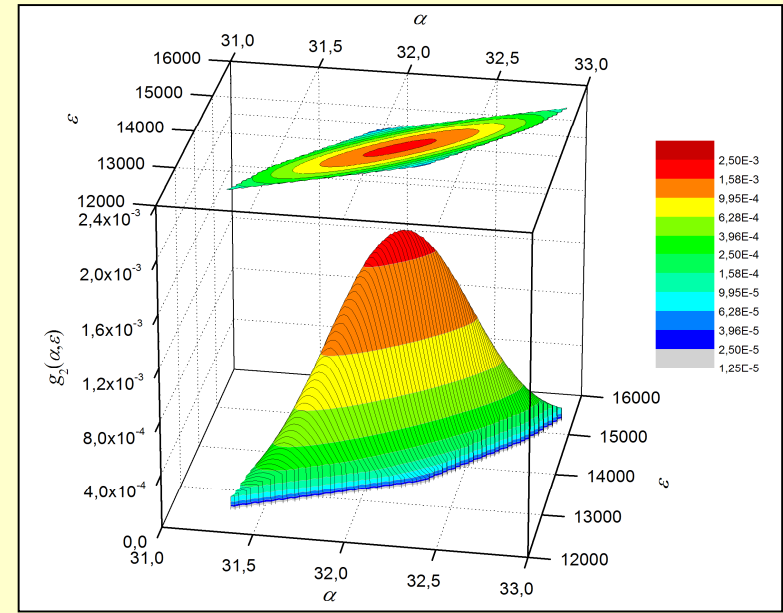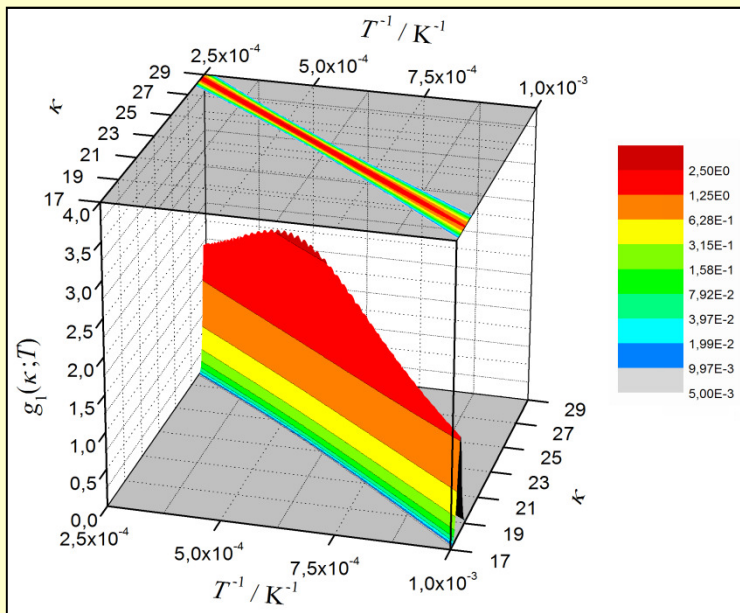
Nagy, T.; Turányi, T. Uncertainty of Arrhenius parameters
Int. J. Chem. Kinet., **43**, 359-378 (2011)

Example: reaction O + N$_2$O → 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 + N₂O → NO + NO
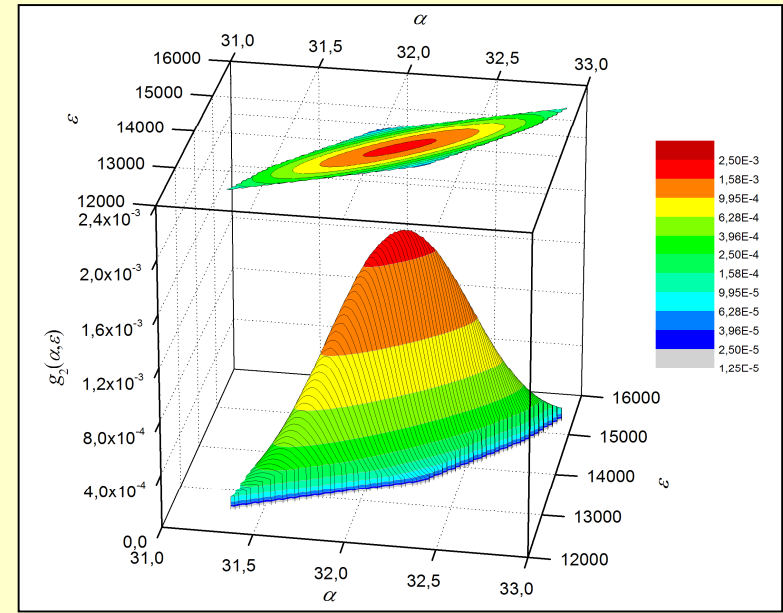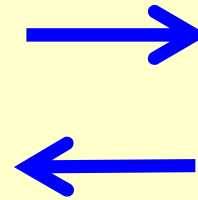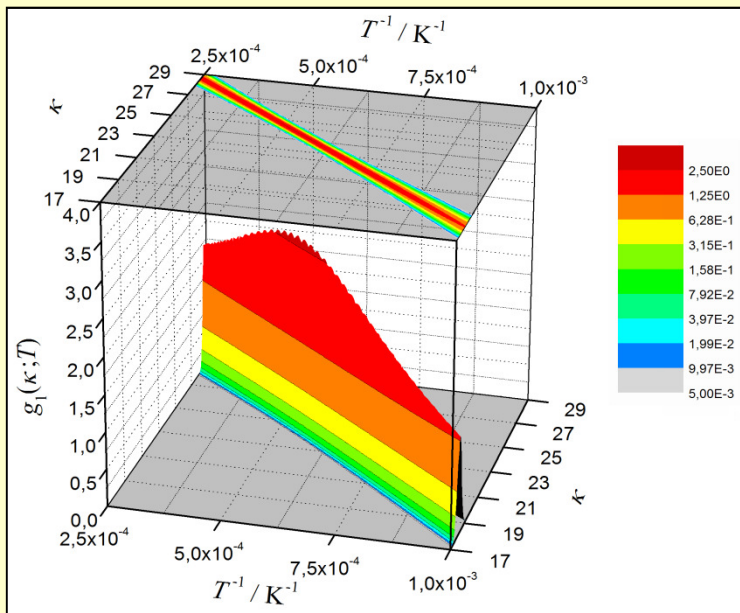
**Temperature dependent
1D normal
probability density function (*pdf*)
of the rate coefficient
(1000 K – 4000 K)**

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

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Calculation of the covariance matrix of the Arrhenius parameters

$$\sigma_\kappa(\theta) = \sqrt{\theta^T \Sigma_p \theta}$$

For the 3-parameter Arrhenius equation:

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

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

→

calculation of a continous
$f(T)$ function

←

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

←

elements of the
covariance matrix
of Arrhenius parameters

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

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

$\Rightarrow$ Reassessment of the uncertainty parameters is needed!

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

We have written a MATLAB + Fortan code called *u-Limits*
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: almost always Baulch *et al.*, 2005

5   MATLAB code: interactive elimination of outliers

6   automatic calculation of „empirical" *f* points at several temperatures
      fitting the elements of the covariance matrix to these points (Fortran code)
      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$_2$)

LP R2: H+O$_2$(+M)=HO$_2$(+M)
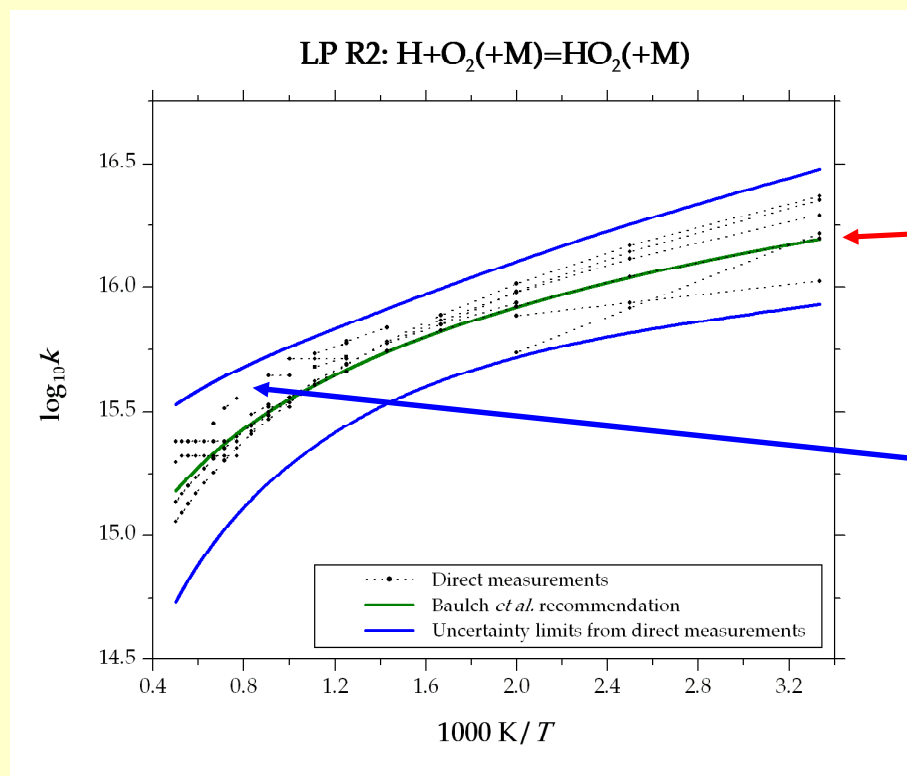
mean line:
Baulch *et al*., 2005

rate expressions from
experiments and theory

Legend:
- Direct measurements
- Baulch *et al.* recommendation
- Uncertainty limits from direct measurements

Axis labels: $\log_{10} k$; $1000\,\mathrm{K}/T$

Example: reaction H + O₂ + M = HO₂ + M
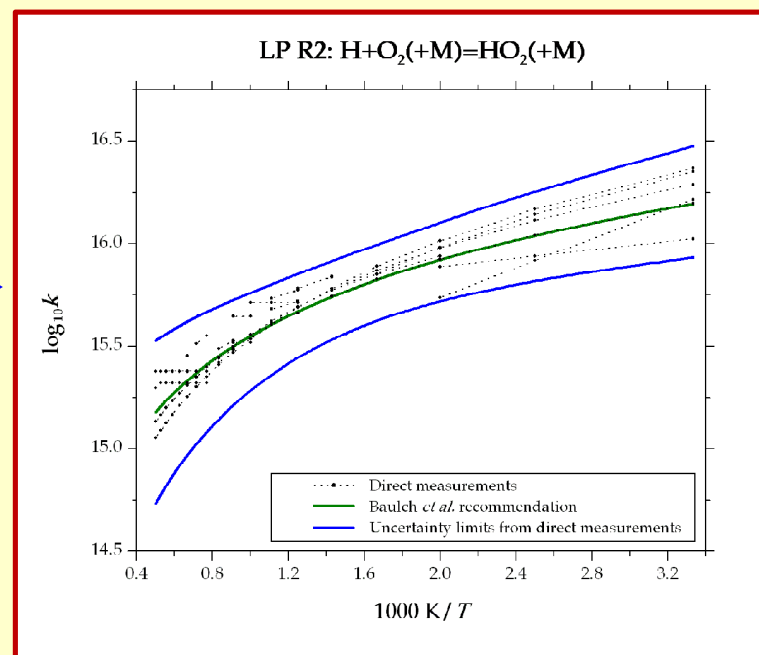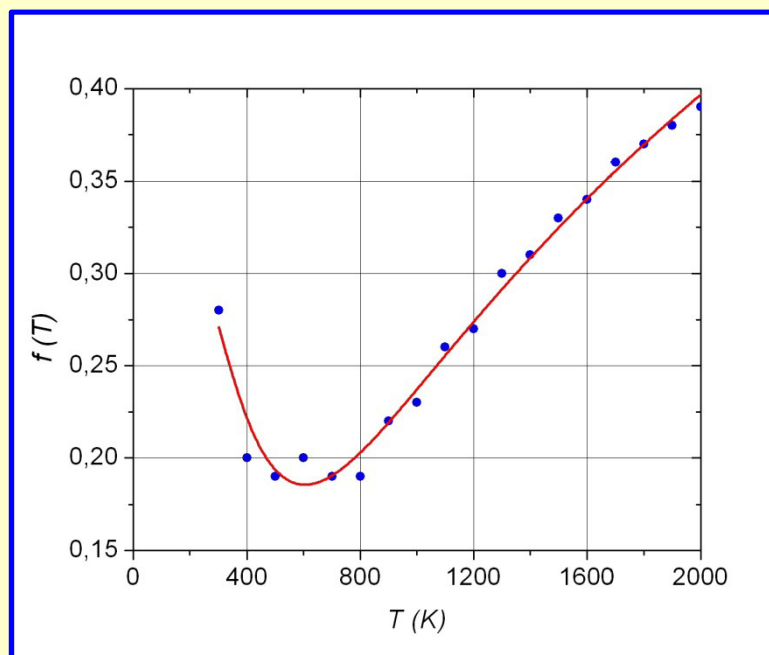
blue dots:
distance from the extreme
experimental/theoretical values
(„empirical f points")

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

Encoding the *pdf* of the Arrhenius parameters

Case A: - only the limits of the uncertainty domain are known
- **multivariate uniform distribution** is assumed
- the limits of ln k are stored

Case B: - many direct measurements
- **multivariate normal distribution** is assumed
- limits of ln $k \Rightarrow$ limits of Arrhenius parameters $\quad \mathbf{p}^{\mathrm{T}} := \begin{bmatrix} \alpha & n & \varepsilon \end{bmatrix}$
     are stored by the parameters of the covariance matrix $\quad \boldsymbol{\Sigma}_{\mathbf{p}}$

$$\boldsymbol{\theta}^{\mathrm{T}} := \begin{bmatrix} 1 & \ln T & -T^{-1} \end{bmatrix} \qquad \sigma_{\kappa}(\boldsymbol{\theta}) = \sqrt{\boldsymbol{\theta}^{\mathrm{T}} \boldsymbol{\Sigma}_{\mathbf{p}} \boldsymbol{\theta}}$$

T. Nagy, T. Turányi
Uncertainty of Arrhenius parameters
Int. J. Chem. Kinet., **43**, 359–378(2011)
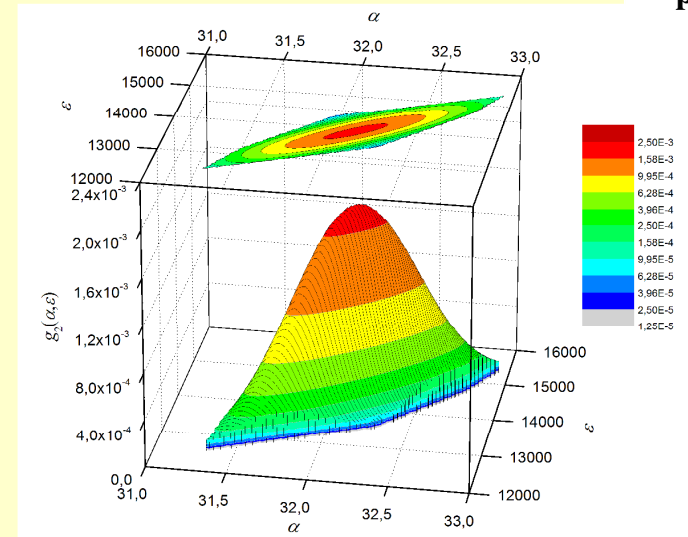
Semi-automatic determination of prior uncertainty

Program **u-Limits**

input: text file containing all direct measurements + TST/ME calculations
related to the selected elementary reaction

output: prior uncertainty of Arrhenius parameters:
pdf of Arrhenius parameters stored in Σ_p
calculation of $f_{prior}(T)$ from Σ_p

Programs called by *u-Limits*:

UBAC (uncertainty band of Arrhenius curves): $f_{original} \rightarrow f_{extreme}$

JPDAP (joint probability density of Arrhenius parameters): $f_{extreme} \rightarrow \Sigma_p$

Revision of the *a priori* uncertainty of 20 elementary reactions

hydrogen combustion

ignition measurements
  in shock tubes 786 data points /54 datasets
  in RCMs   166 data points /9 datasets
flame velocity   631 data points /71 datasets
PSR data   152 data points /9 datasets

wet CO combustion

ignition measurements
  in shock tubes 532 data points /50 datasets
  in RCMs   444 data points /46 datasets
flame velocity   1711 data points /175 datasets
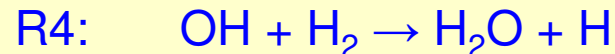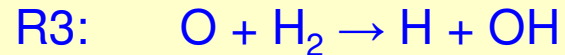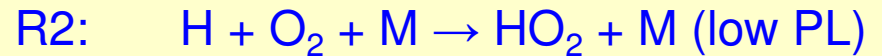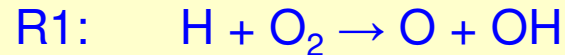PSR data   54 data points /9 datasets

local sensitivity analysis:

sensitivity of each simulated data point
with respect to the *A*-factors

These elementary reactions were
in the top 10 at all conditions
in hydrogen and wet CO
combustion systems $\Rightarrow$

R1: $H + O_2 \rightarrow O + OH$
R2: $H + O_2 + M \rightarrow HO_2 + M$ (low PL)
R3: $O + H_2 \rightarrow H + OH$
R4: $OH + H_2 \rightarrow H_2O + H$
R5: $H_2O_2 + H \rightarrow H_2 + HO_2$
R6: $H + HO_2 \rightarrow OH + OH$
R7: $H + HO_2 \rightarrow H_2 + O_2$
R8: $HO_2 + OH \rightarrow H_2O + O_2$
R9: $OH + OH \rightarrow H_2O_2$ (high PL)
            $OH + OH + M \rightarrow H_2O_2 + M$ (low PL)
R10: $H + OH + M \rightarrow H_2O + M$ (low PL)
R11: $OH + OH \rightarrow H_2O + O$
R12: $H + H + M \rightarrow H_2 + M$ (low PL)
R13: $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
R14: $H_2O_2 + H \rightarrow H_2O + OH$
R15: $CO + OH \rightarrow CO_2 + H$
R16: $HCO + M \rightarrow H + CO + M$
R17: $CO + O_2 \rightarrow CO_2 + O$
R18: $H + O + M \rightarrow OH + M$ (low PL)
R19: $H_2O_2 + OH \rightarrow HO_2 + H_2O$
R20: $HCO + O_2 \rightarrow HO_2 + CO$
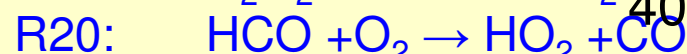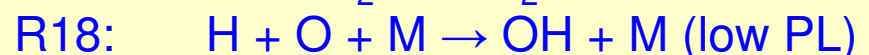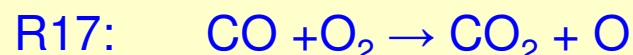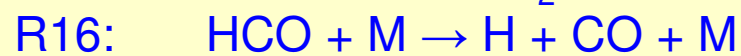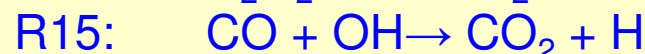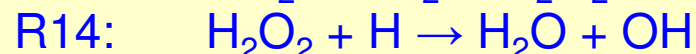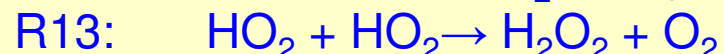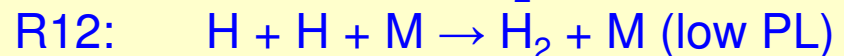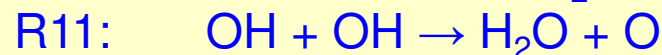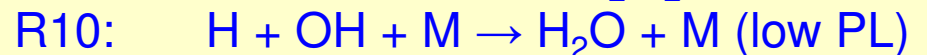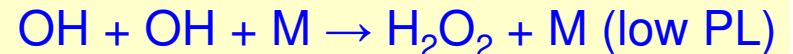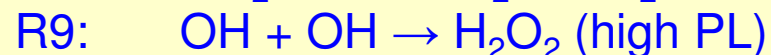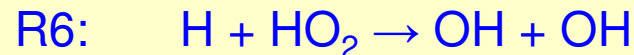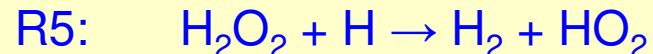
Prior uncertainty for 22 reactions

The theory above was applied to the 22 most sensitive elementary reactions of the hydrogen/syngas combustion system.
These are the obtained $f_{prior}(T)$ functions:
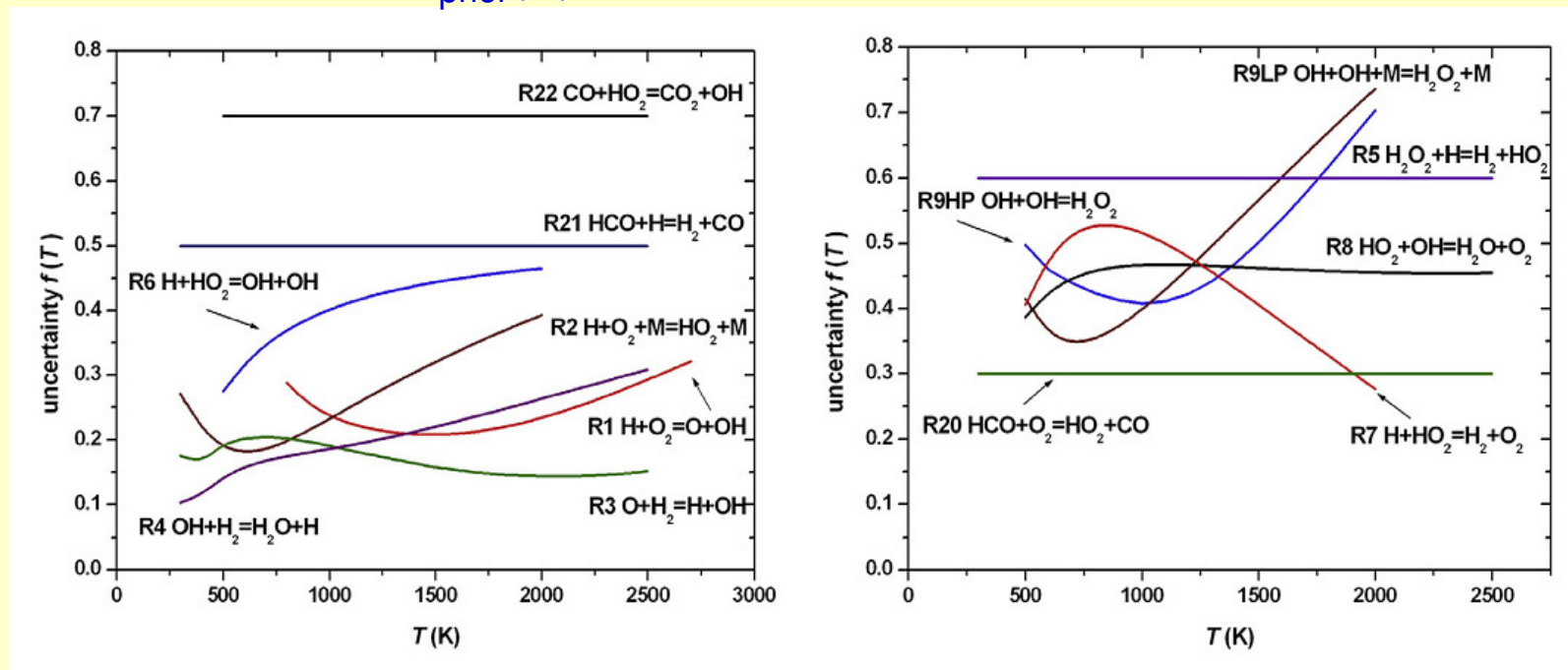
T. Nagy, É. Valkó, I. Sedyó, I. Gy. Zsély, M. J. Pilling, T. Turányi:
Uncertainty of the rate parameters of several important elementary reactions
of the H_2 and syngas combustion systems
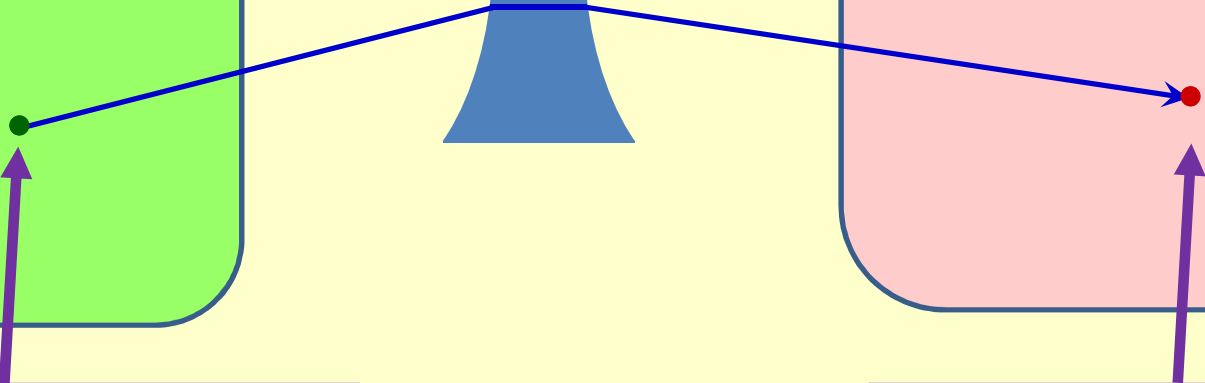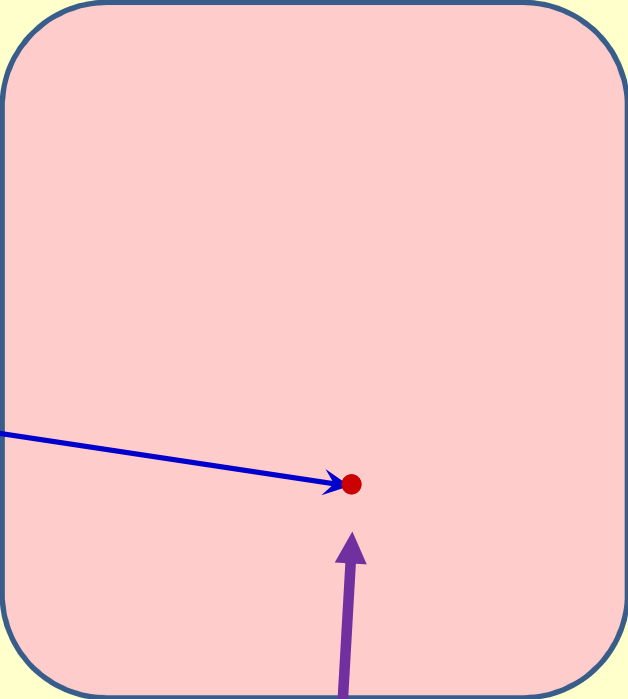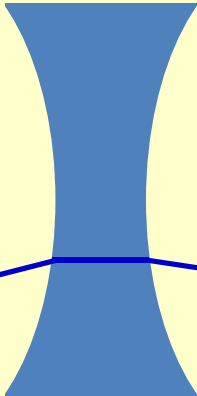*Combust. Flame*, **162**, 2059-2076 (2015)
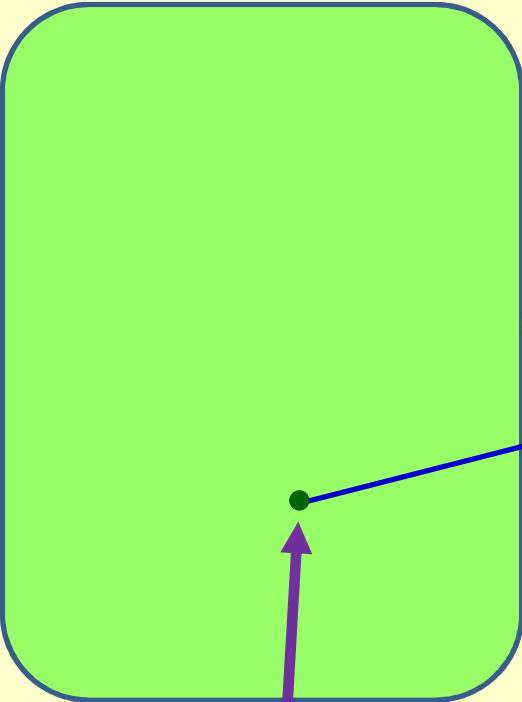
Parameters and model results

space of parameters

space of model results

model

nominal parameter set
of the model

nominal result
of the model

Uncertainty of model parameters

space of parameters

model

space of model results

prior uncertainty domain of model parameters
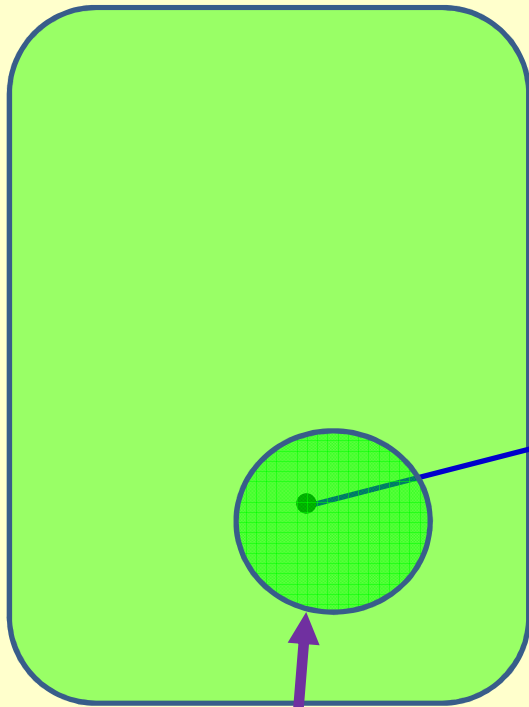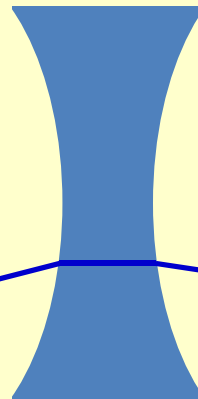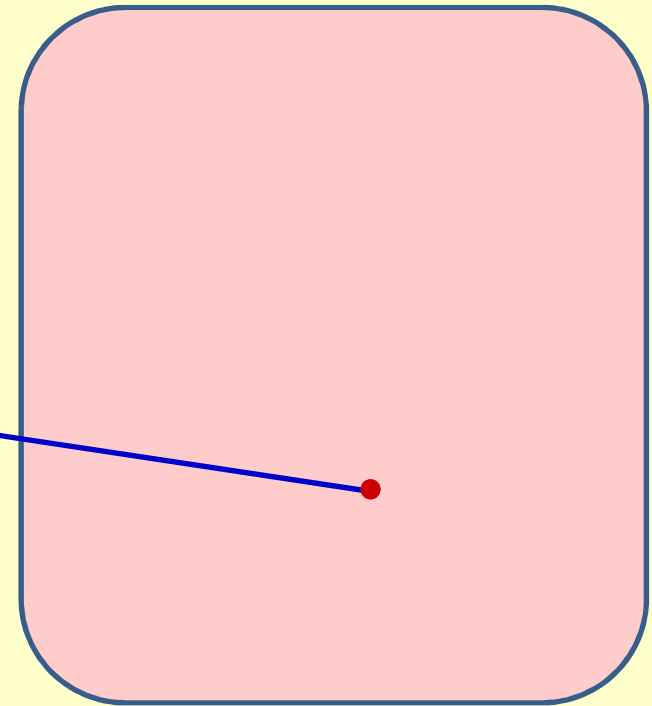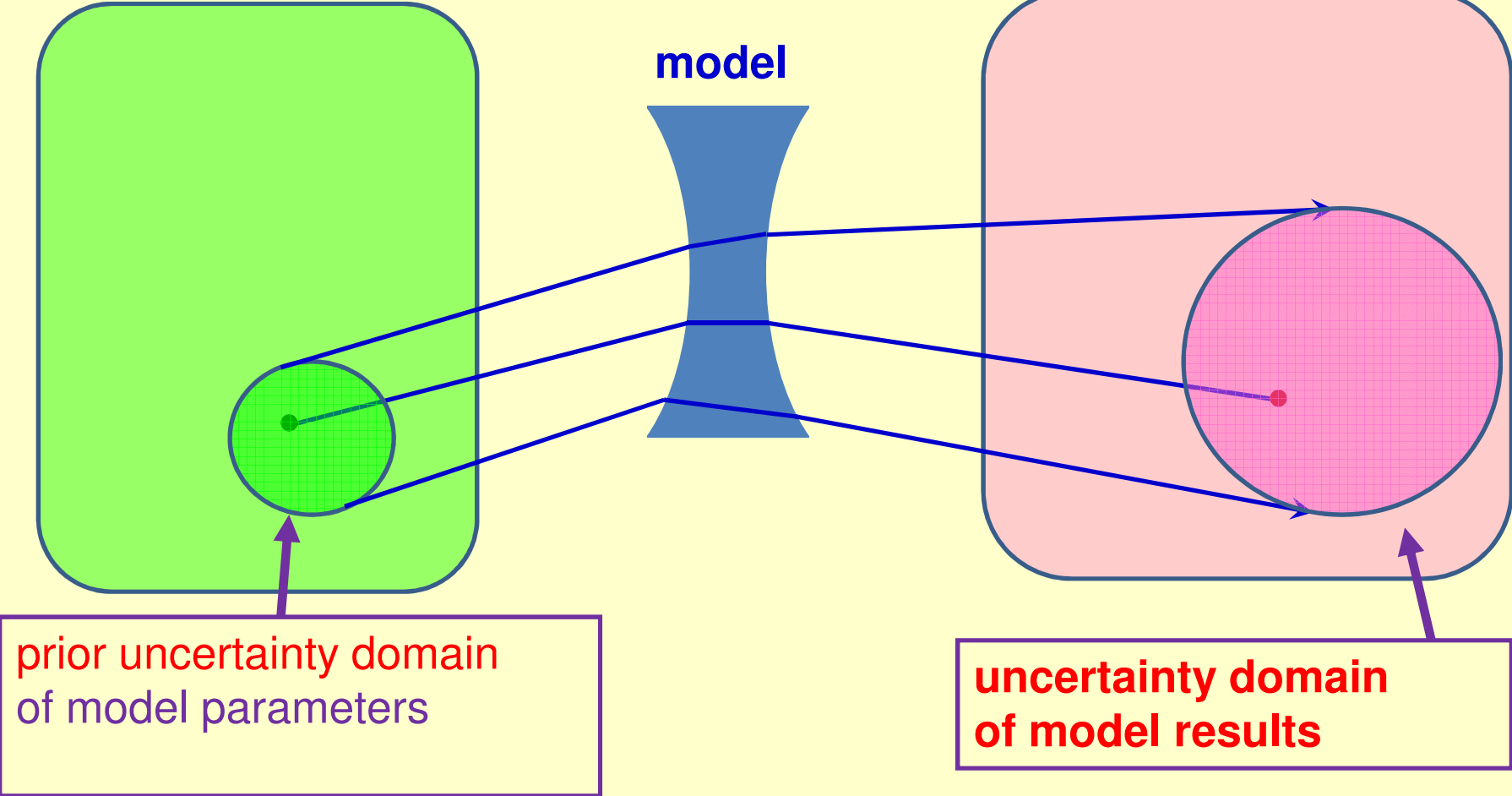
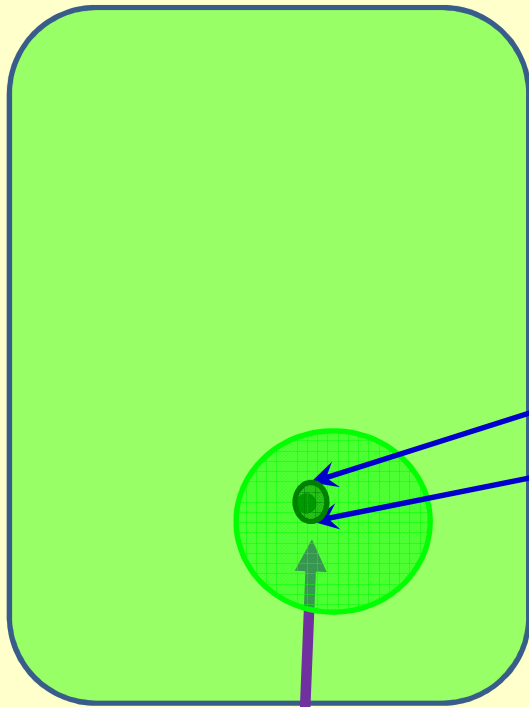# Uncertainty of model results

space of parameters

space of model results

model

prior uncertainty domain
of model parameters

**uncertainty domain
of model results**

Posterior uncertainty of parameters

space of parameters

model

space of model results
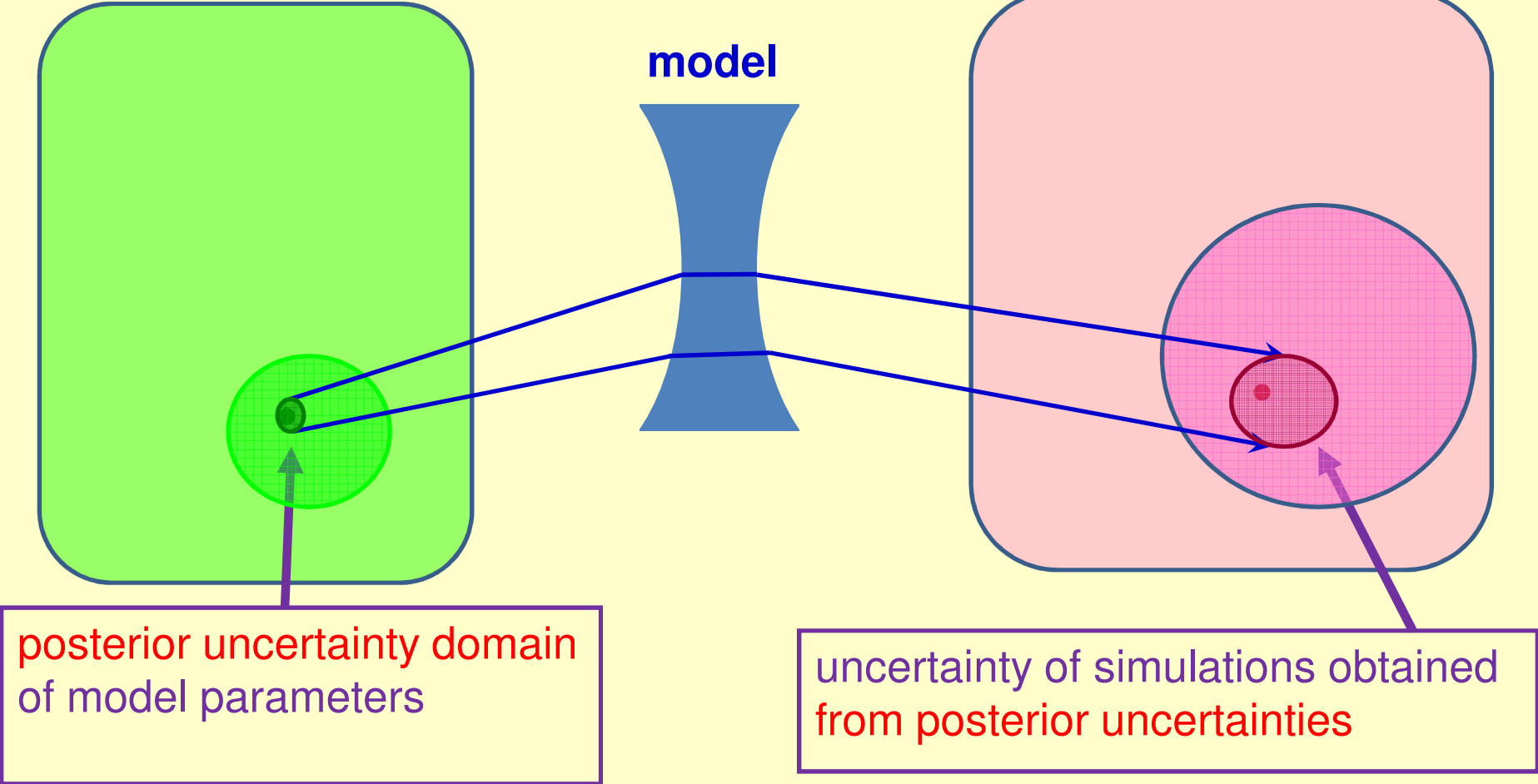
posterior uncertainty domain
of model parameters

uncertainty of simulations obtained
from posterior uncertainties

Problems with the *prior* uncertainty

The principal aim is not to exclude possible parameters:
⇒ too wide limits to get a cautious uncertainty estimation

Deals with the elementary reactions individually:
⇒ cannot define joint uncertainties

Better uncertainty is needed, which is

- based on all available scientific information
- results of mathematical statistical calculations
- defines the joint uncertainty of the parameters

⇒ ***posterior*** **uncertainty domain of the rate parameters**

Determination of the *posterior* uncertainty

of the reaction rate parameters

Mechanism optimisation

1   all indirect measurement data should be collected
       that are applicable for testing a mechanism.

2   sensitivity analysis for finding the important reaction steps
       (simulated data points wiith respect to the rate parameters)
       the rate parameters of these reactions will be optimised

3   determination of the *prior* uncertainty of the rate parameters
       (= determination of the domain of allowed parameter values)

4   all reliable direct measurement data and high level theoretically calculated
       rate coefficients related to the important reactions are collected

5   global parameter optimisation
       considering both the indirect and direct measurement data
          ⇒ new rate parameters with physical meaning
          ⇒ ***a posteriori* uncertainty domain of rate parameters**

Turányi T, Nagy T, Zsély IGy, Cserháti M, Varga T, Szabó B,
Sedyó I, Kiss P, Zempléni A, Curran H J
Determination of rate parameters based on both direct and indirect measurements.
Int. J. Chem. Kinet. **44**, 284–302 (2012)

Determination of posterior uncertainties
for a syngas combustion mechanism

Posterior uncertainties

Results of optimization:
fitting to both indirect and direct experimental data

Hydrogen combustion data

Extensive review of the literature was carried out
- Ignition delays – shock tube   786 datapoints in 54 datasets
- Ignition delays – RCM   229 datapoints in 20 datasets
- Laminar flame velocities   631 datapoints in 73 datasets
- Species profiles – JSR   149 datapoints in 9 datasets
- Species profiles – flow reactor   372 datapoints in 16 datasets

Wide range of conditions
- Temperature: 800 K – 2300 K
- Pressure   0.1 bar – 65 bar
- Equivalence ratio   0.2 – 5.0

Syngas combustion data

Extensive review of the literature was carried out
- Ignition delays – shock tube   654 datapoints in 62   datasets
- Ignition delays – RCM   387 datapoints in 40   datasets
- Laminar flame speeds   1963 datapoints in 202 datasets
- Species profiles – JSR   54   datapoints in 3   datasets
- Species profiles – flow reactor   633 datapoints in 44   datasets
- Species profiles – shock tube   436 datapoints in 7   datasets

Wide range of conditions
- Temperature: 800 K – 2000 K (max. 2800 K)
- Pressure   0.5 bar – 50 bar (max. 500 bar)
- Equivalence ratio 0.35 – 5.0
- H_2/CO ratio   0.1 – 3.0

Initial mechanism –

C/H/O reactions of the Kéromnès *et al.* mechanism
  A. Kéromnès, W.K. Metcalfe, K.A. Heufer, N. Donohoe, A.K. Das, C.-J. Sung, J. Herzler, C. Naumann, P. Griebel,
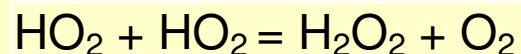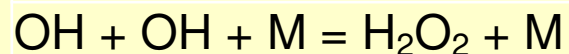 O. Mathieu, M.C. Krejci, E.L. Petersen, W.J. Pitz, H.J. Curran, Combust. Flame 160 (2013) 995–1011.
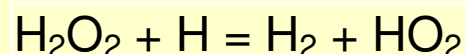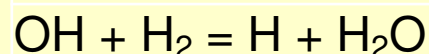Our recently published optimised hydrogen combustion mechanism
  T. Varga, T. Nagy, C. Olm, I. Gy. Zsély, R. Pálvölgyi, É. Valkó, G. Vincze, M. Cserháti, H. J. Curran, T. Turányi
  Proc. Comb. Inst., **35**, 589-596 (2015)

Reactions selected for optimisation

18 elementary reaction steps selected based on local sensitivity analysis

The third body collision efficiencies for all major species were investigated – Ar, He, H_2, O_2, H_2O, CO, CO_2

$CO + OH = CO_2 + H$
$CO + O_2 = CO_2 + O$
$CO + HO_2 = CO_2 + OH$
$HCO + M = H + CO + M$
$HCO + H = CO + H_2$
$OH + OH = O + H_2O$
$H + H + M = H_2 + M$

$H + O_2 = O + OH$
$H + O_2 + M = HO_2 + M$
$O + H_2 = H + OH$
$HO_2 + H = OH + OH$
$HO_2 + OH = H_2O + O_2$
$H + OH + M = H_2O + M$
$H + HO_2 = H2 + O_2$
$OH + H_2 = H + H_2O$
$H_2O_2 + H = H_2 + HO_2$
$OH + OH + M = H_2O_2 + M$
$HO_2 + HO_2 = H_2O_2 + O_2$
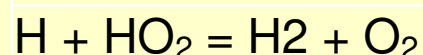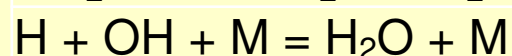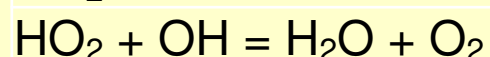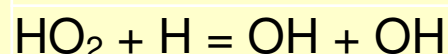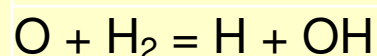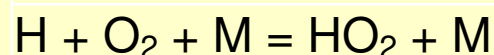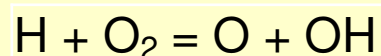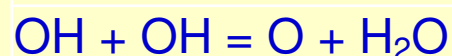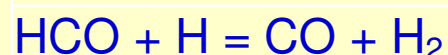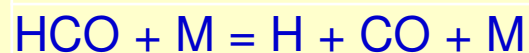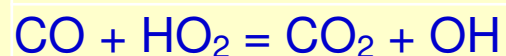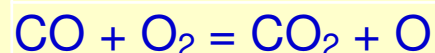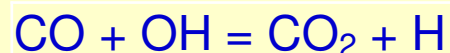
2275 directly measured rate coefficient values in 85 datasets were also used

Optimisation and uncertainty calculation

Optimisation - minimisation of this error function:

$$E(\mathbf{p}) = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{N_i} \sum_{j=1}^{N_i} \left(\frac{Y_{ij}^{mod}(\mathbf{p}) - Y_{ij}^{exp}}{\sigma(Y_{ij}^{exp})} \right)^2$$

y_{ij} measured/calculated rate coefficient OR measured/calculated ignition time/flame velocity in data point j of data series i

$$Y_{ij} = \begin{cases} y_{ij} & \text{if } \sigma(y_{ij}^{exp}) \approx \text{constant} \\ \ln y_{ij} & \text{if } \sigma(\ln y_{ij}^{exp}) \approx \text{constant} \end{cases}$$

σ standard deviation of the measured data

N_i number of data points in data series i

N number of data series (different experiments)

Calculation of the covariance matrix of the estimated parameters:

Covariance matrix of experiments

Discrepancy between experiments and model

$$\mathbf{\Sigma_p} = \left[(\mathbf{J_o^T W \Sigma_Y^{-1} J_o})^{-1} \mathbf{J_o^T W \Sigma_Y^{-1}} \right] (\mathbf{\Sigma_Y + \Sigma_\Delta}) \left[(\mathbf{J_o^T W \Sigma_Y^{-1} J_o})^{-1} \mathbf{J_o^T W \Sigma_Y^{-1}} \right]^T$$

The obtained rate parameters

Optimized subset of reactions		Optimized parameters		
		ln A	n	E/R
R24	$CO + OH = CO_2 + H$	9.717	2.221	-694.7
R1	$H + O_2 = O + OH$	36.16	-0.4859	8116
R9	$H + O_2 + M = HO_2 + M$	45.41	-1.373	-
R2	$O + H_2 = H + OH$	14.04	2.270	3501
R11	$HO_2 + H = OH + OH$	31.69	-	86.07
R13	$HO_2 + OH = H_2O + O_2$	27.59	0.4201	-477.4
R8	$H + OH + M = H_2O + M$	55.66	-2.538	60.79
R10	$H + HO_2 = H2 + O_2$	14.57	2.113	-817.7
R3	$OH + H_2 = H + H_2O$	16.40	1.878	1586
R18	$H_2O_2 + H = H_2 + HO_2$	46.03	-1.925	4743
R16	$OH + OH + M = H_2O_2 + M$	42.14	-1.178	-2150
R23	$CO + O_2 = CO_2 + O$	28.69	-	24005
R25	$CO + HO_2 = CO_2 + OH$	16.53	1.680	9139
R15	$HO_2 + HO_2 = H_2O_2 + O_2$	35.01	-	7826
R26	$HCO + M = H + CO + M$	24.62	0.9596	7368
R28	$HCO + H = CO + H_2$	31.79	-	-
R4	$OH + OH = O + H_2O$	11.35	2.2642	-898.2
R5	$H + H + M = H_2 + M$	43.05	-1.213	308.0

Units are cm, mole, s, K

Results of optimization

Set of optimized rate parameters

Covariance matrix of all optimized parameters

this is the basic *posterior* uncertainty information
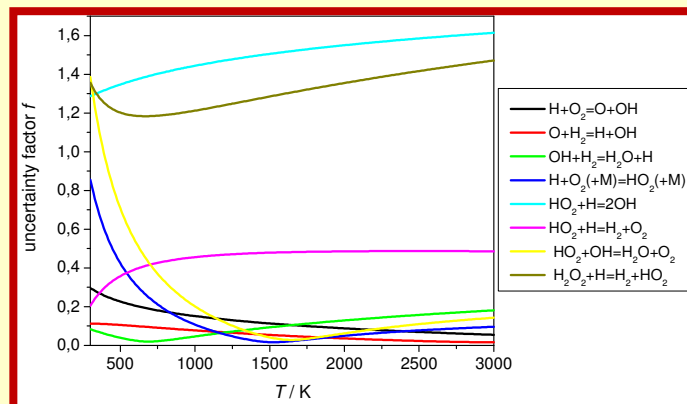
posterior $f(T)$ uncertainty function of rate coefficients
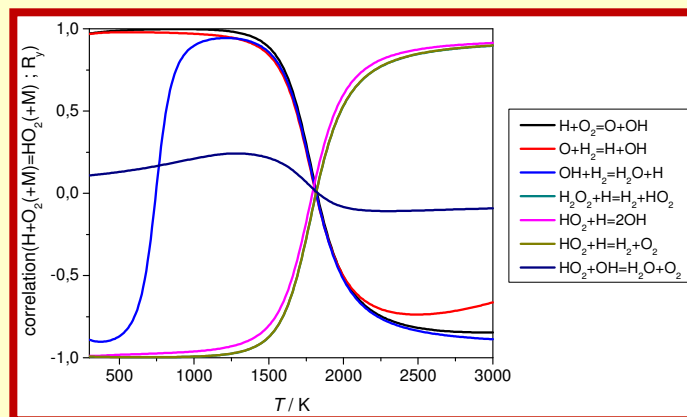
Correlation of rate coefficients

prior vs. posterior uncertainty

for each reaction:
the *posterior* region was narrower
and typically within the *prior* uncertainty region.

LP R2: $H+O_2(+M)=HO_2(+M)$
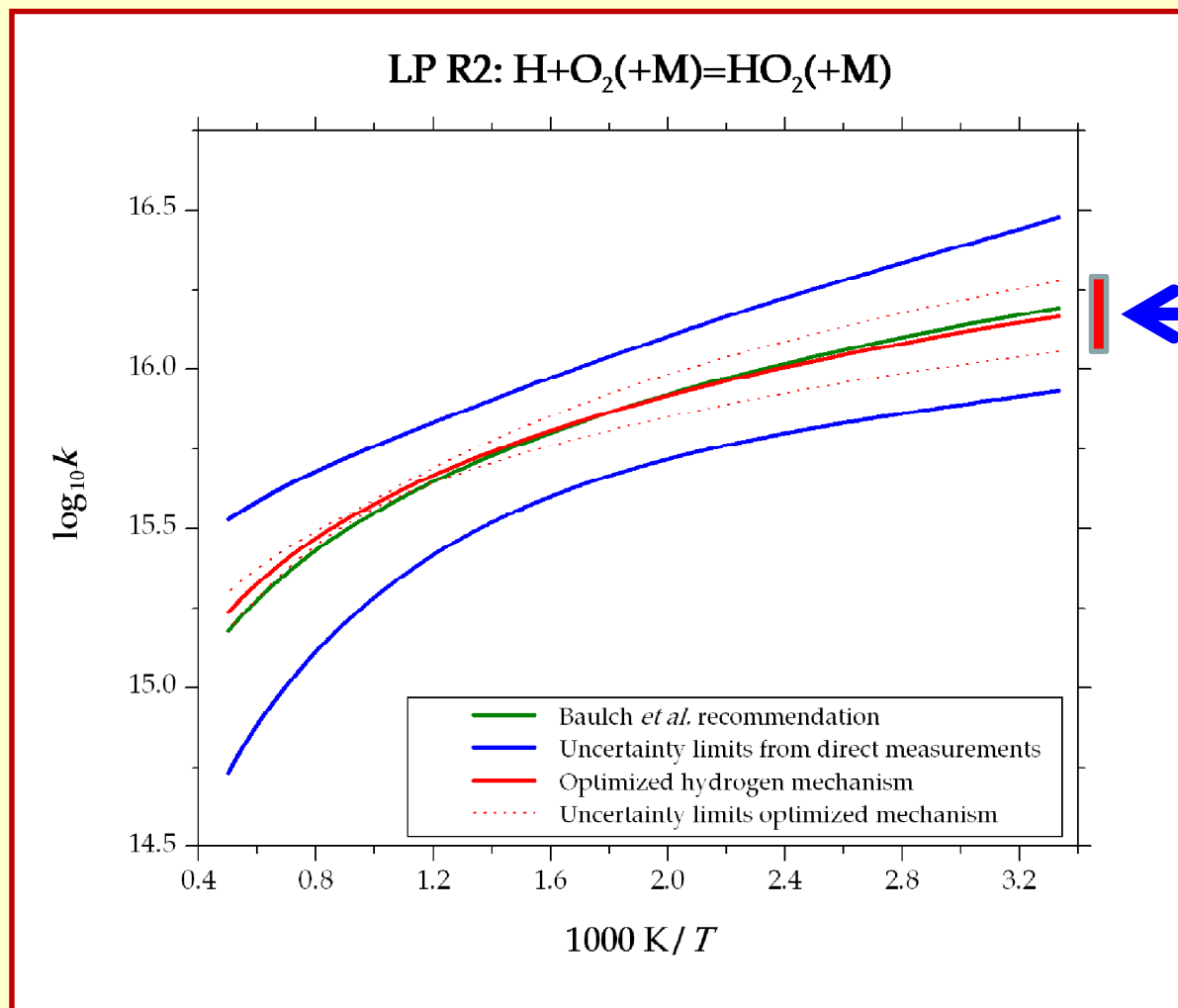
a posteriori range of uncertainty

Baulch *et al.* recommendation
Uncertainty limits from direct measurements
Optimized hydrogen mechanism
Uncertainty limits optimized mechanism

$\log_{10} k$

$1000\ \mathrm{K}/T$

56

Testing the optimised mechanism

- Laminar flame speed measurements of Santner *et al.* (2013)
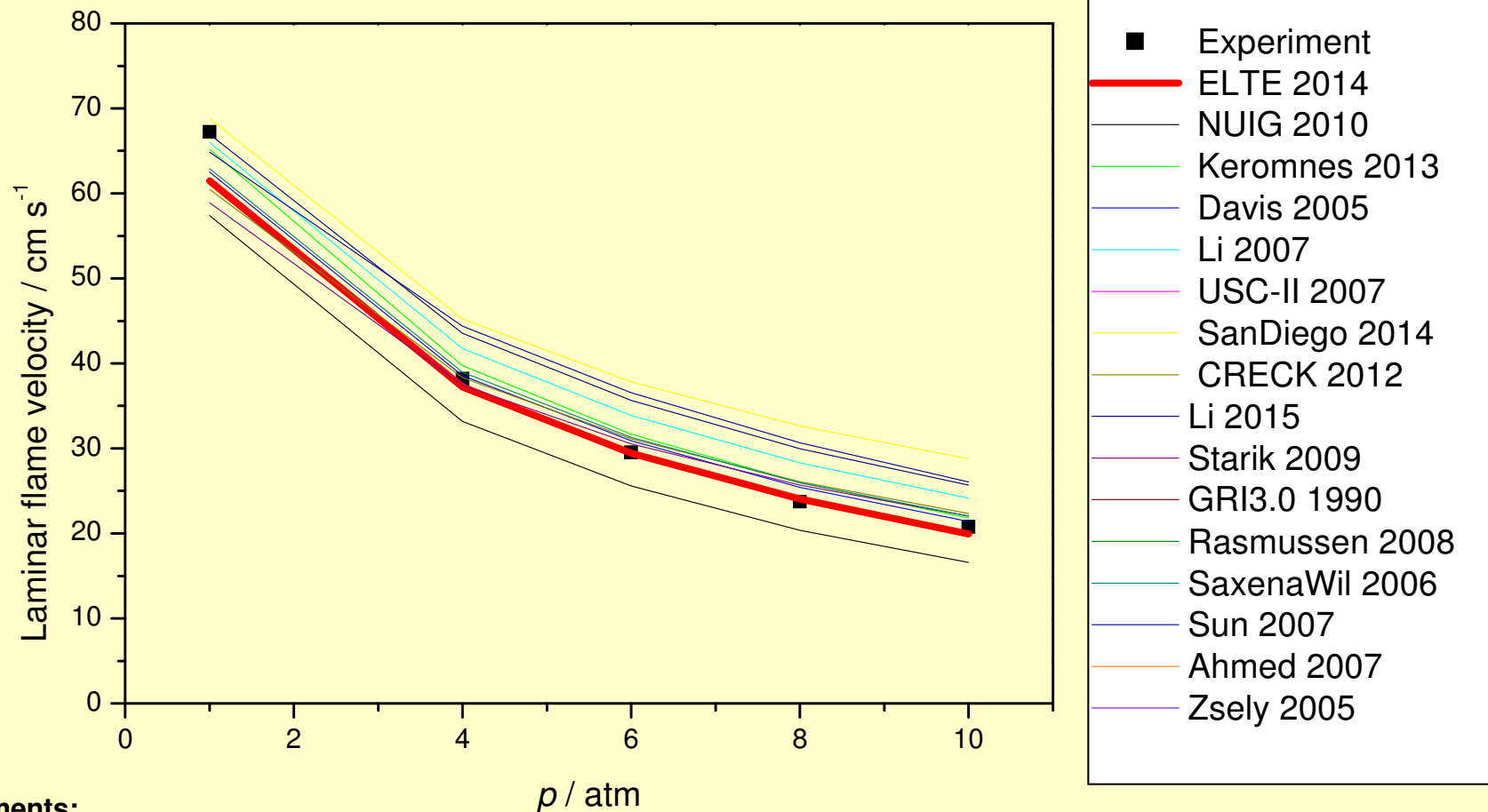
experiments:
Santner *et al., Proc. Combust. Inst.*, **34**, 439-446 (2013) T_0 = 295 K equivalence ratio = 0.85 H$_2$:CO ratio = 1:1   5% steam added

Testing the optimised mechanism 2

- Shock tube study of Thi *et al.* (2014)

experiments:
Thi *et al. Can. J. Chem. Eng.,* **92**, 861-870 (2014) $T = 902– 1161$ K; $p = 1.6$ bar; equivalence ratio= 1 H_2:CO ratio: 2.3:1

Comparison with other syngas mechanisms

Syngas combustion

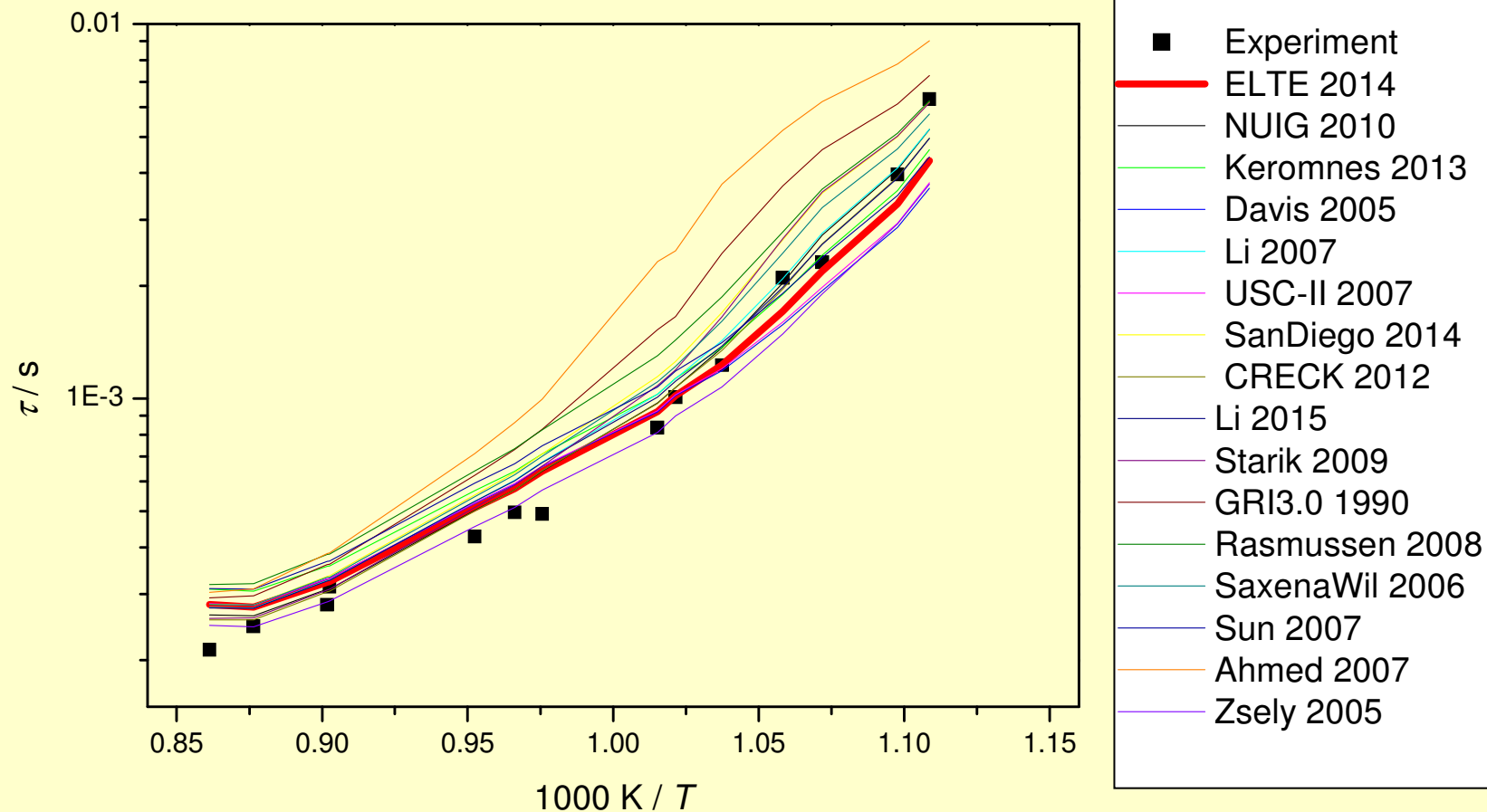| Mechanism	Average error function					
	IDT	Conc	Flame noHe	Flame wHe	Total noHe	Total wHe
ELTE Syngas 2016	**14.83**	**7.95**	**4.95**	**4.84**	**8.43**	**8.08**
NUIG NGM 2010	26.52	11.72	7.59	7.84	**14.05**	**13.69**
Kéromnès 2013	38.09	21.34	6.60	6.29	**18.33**	**17.20**
Davis 2005	52.04	13.49	4.26	4.36	**20.43**	**19.19**
POLIMI 2014	45.28	29.17	5.49	5.89	**20.93**	**19.93**
Li 2015 (PROCI)	19.80	105.73	5.27	5.92	**22.27**	**21.30**
Li 2007	50.77	30.11	5.58	5.79	**22.82**	**21.57**
USC 2007 II	64.17	10.78	5.17	-	**24.41**	-
San Diego 2014	30.38	50.92	15.81	16.20	**24.73**	**24.25**
Starik 2009	36.04	75.02	15.58	14.66	**29.37**	**27.71**
GRI 3.0 1999	77.23	55.56	5.49	-	**34.24**	-
Rasmussen 2008	87.12	74.65	16.15	-	**45.70**	-
Saxena Williams 2006	77.51	162.54	5.31	5.39	**47.47**	**44.14**
Sun 2007	133.69	84.05	5.74	6.85	**55.65**	**52.32**
No. of datasets	94	37	168	194	299	325
No. of data points	938	777	1649	1879	3364	3594

Conclusions

- The uncertainty parameter *f* values given in the evaluations
  belong to separate temperature values/intervals and
  are not in accordance with the Arrhenius expression of *k*

  A procedure was suggested **to obtain consistent prior *f* values**
  UBAC: $f_{original} \rightarrow f_{extreme}$

- The $T{-}f_{extreme}$ table can be transformed (using program JPDAP)
  to the **covariance matrix Σ_p of the Arrhenius parameters** (6 parameters)

- Σ_p can be used to restore prior **uncertainty parameter f_{prior} (*T*)**

- Σ_p defines the **prior uncertainty domain of Arrhenius parameters**,
  to be used in mechanism optimization studies

- **Prior uncertainty was determined for 22 syngas elementary reactions**

- A new **optimised syngas combustion model** was developed

- The **performance of the model was tested** against
  (almost) all available indirect experimental data

- New rate parameters of 18 elementary reaction steps
  were obtained with **joint posterior uncertainty domain**

T. Varga, C. Olm, T. Nagy, I. Gy. Zsély, É. Valkó, R. Pálvölgyi, H. J. Curran, T. Turányi
Development of a joint hydrogen and syngas combustion mechanism based on an optimization
approach, *Int.J.Chem.Kinet.*, *in press* (2016)

Summary

prior uncertainty of the rate parameters
- determined for each elementary reaction separately
- uncertainty parameter f is available, but
    its temperature dependence is often missing
- reevaluation of each elementary reaction is needed

Resuls of reevaluation:
- realistic $f(T)$ function
- domain of uncertainty of the Arrhenius parameters

It is important for a practicising kineticist:
which are the limits of changes in the Arrhenius parameters.

**Program suite *u-Limits* + UBAC + JPDAP
was written to make the calculation of
the uncertainty domain of the Arrhenius parameter
a semiautomatic process.**

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Summary 2

***posterior* uncertainty of the rate parameters**
   - by-product of mechanism optimization
   - should be done for a group of related reactions
   - should be interpreted as a joint domain of uncertainty
   - reflects all information about the system:
         direct and indirect measurements,
         high-level theoretical calculations

Code Optima++ for optimization studies provides

         „raw" uncertainty information:
                  covariance matrix of the optimized parameters
         „processed" uncertainty information:
                  $f(T)$ functions + temperature dependent correlations

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Thank you for your attention!