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

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Rate coefficient uncertainties

Uncertainty factor $f_j$ as defined in data evaluations (Tsang, Warnatz, Baulch, Konnov):

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

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

$k_j^0$ 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 $3\sigma$ from $\ln k^0$

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

$1\sigma$ uncertainty limit (assuming that $u$ corresponds to $3\sigma$): $l = 10^{f/3}$
Uncertainty of \( k \) at a given temperature

Uncertainty of (direct) rate coefficient measurements:

- very high quality data: uncertainty factor \( u = 1.26 \iff f = 0.1 \iff \pm 8\% (1\sigma) \)
- typical good data: uncertainty factor \( u = 2.00 \iff f = 0.3 \iff \pm 26\% (1\sigma) \)
- typical data: uncertainty factor \( u = 3.16 \iff f = 0.5 \iff \pm 47\% (1\sigma) \)

(high level) theoretical determinations:

- TST/master equation calculations

- best systems: uncertainty factor \( u = 2.00 \iff f = 0.3 \iff \pm 26\% (1\sigma) \)
- multi well, main channels: uncertainty factor \( u = 3.16 \iff f = 0.5 \iff \pm 47\% (1\sigma) \)
- multi well, minor channels: uncertainty factor \( u = 10.00 \iff f = 1.0 \)


J. Prager, H. N. Najm, J. Zádor: Uncertainty quantification in the *ab initio* rate-coefficient calculation for the \( \text{CH}_3\text{CH(OH)CH}_3+\text{OH} \rightarrow \text{CH}_3\text{C.(OH)CH}_3+\text{H}_2\text{O} \) reaction, *Proc. Combust. Inst.*, **34**, 583-590 (2013)
Temperature dependence of thermodynamic data

**NASA polynomials**

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

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

\[
\frac{S^\theta}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7
\]
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
      → reaction enthalpy → enthalpy of formation
    • measuring ionization energy by mass spectrometry
Uncertainty of thermodynamic data 2

Typical uncertainty of $\Delta H_f^\circ (1\sigma)$:

- molecules and small radicals: 0.1-0.5 kJ/mole
  - *e.g.* CO = 0.17 kJ/mole, $\text{CH}_4$ = 0.4 kJ/mole, $\text{CH}_3$ = 0.4 kJ/mole

- large radicals: 1.0 – 5.0 kJ/mole
  - *e.g.* $\text{HO}_2$ = 3.35 kJ/mole, $\text{CH}_2\text{OH}$ = 4.2 kJ/mole

- less known radicals: 8-10 kJ/mole
  - *e.g.* HCCO = 8.8 kJ/mole, $\text{CH}_2\text{HCO}$ = 9.2 kJ/mole
Determination of the enthalpies of formation

Methods for the determination of enthalpies of formation $\Delta H_f$:

1) direct experimental determination:
   calorimetry; synthesis from reference state elements
   $\text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}$ 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 $\Delta H_f$ after a chain of calculations
Determination of the enthalpies of formation 2

„4) determination of $\Delta H_f$ after a chain of calculations”
- starting from directly determined $\Delta H_f$ values

$$\Delta f H^\theta = \sum_j v_j \ H_f^\theta (j)$$

a) combining it with a $\Delta_f H^\theta$ value provides a new $\Delta H_f^\theta$ value
⇒ indirectly determined $\Delta H_f^\theta$

b) GO TO a) until we get the required $\Delta H_f^\theta$

⇒ the chain of calculation provides the required $\Delta H_f^\theta$

PROBLEMS:
- Going on in the chain of calculations, the errors are accumulated
  $\Delta H_f^\theta$ values at the end of a long chain are not very accurate.
- $\Delta H_f^\theta$ values for the same species can be obtained at the ends of two different calculation chains ⇒ different $\Delta H_f^\theta$ values are obtained ?????
Idea of Branko Ruscic

the determination of many enthalpies of formation $\Delta H_f^\theta$ in one step:

using $n$ direct experimental determination:  

$H_f^\theta(j) = A_j \quad j = 1, \ldots , n$

using $m$ measured $\Delta_r H^\theta$ values:  

$\Delta_r H_i^\theta = \sum_j v_{ij} H_f^\theta(j) \quad j = n+1, \ldots , n+m$

The aim is the determination of $k$ values of $\Delta H_f^\theta$:

- if $k > n+m$  \Rightarrow  not enough info
- if $k < n+m$  \Rightarrow  overdetermined linear algebraic system of equations  
  \Rightarrow  determination of the $\Delta H_f^\theta$ values by the least squares method

If the errors of the measurements are also taken into account  

\Rightarrow  weighted least squares method

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 continuously adding new measurements and sometimes publishes $\Delta_r^\theta H$ 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)

Using thermodynamic data in combustion simulations

$\Delta H_f \Rightarrow$ 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

$\Delta S \Rightarrow$ calculation of $\Delta G = \Delta H - T \Delta S$
  $\rightarrow$ calculation of the equilibrium constant
  $\rightarrow$ calculation of the rate coefficient of reverse reactions
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

Determination of rate parameters based on both direct and indirect measurements
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) ±10 % (1σ)
  typical data uncertainty (3σ) factor of 3.0 (f=0.5) ±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 $A, n, E$, 3\textsuperscript{rd} body collision efficiencies, (parameters of pressure 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):

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

$f_1, f_2, f_3, \ldots$ corresponds to the actual scatter of measurements in this temperature region. We will call them $f_{\text{original}}$ values.

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

The $f_{\text{original}}$ 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 $f_{\text{extreme}}$.
Domain of uncertainty of Arrhenius parameters

The $f_{\text{extreme}}(T)$ 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 $\ln A$, $E/R$
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 $\ln A, \frac{E}{R}$
3D domain of Arrhenius parameters

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

three Arrhenius parameters $\alpha = \ln A$, $n$, $\varepsilon = E/R$

the extreme Arrhenius curves = vertices of the convex hull
Uncertainty parameter $f$

Definition of uncertainty factor $f$:

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

Calculation of the variance of $\ln k$ from uncertainty factor $f$:

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

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

Instead of temperature dependent $\sigma(\ln k)$

the covariance matrix of the Arrhenius parameters is needed!

extended Arrhenius expression:

$$k(T) = A T^n \exp\left(- \frac{E}{RT}\right)$$

linearized form:

$$\ln\{k(T)\} = \ln\{A\} + n \cdot \ln\{T\} - \left\{\frac{E}{R}\right\} \cdot \{T\}^{-1}$$
Relation between the $\sigma$ of the rate coefficient and the covariance matrix of the Arrhenius parameters

Matrix-vector form of the linearized Arrhenius equation:

$$\mathbf{p}^T := \begin{bmatrix} \alpha & n & \varepsilon \end{bmatrix} \quad \mathbf{\theta}^T := \begin{bmatrix} 1 & \ln \theta & -\theta^{-1} \end{bmatrix}$$

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

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

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

$$\sigma_k(\theta) = \sqrt{\mathbf{\theta}^T \Sigma_p \mathbf{\theta}}$$

$\Rightarrow$ the temperature dependent standard deviation of $k$ can be calculated from a quadratic form.

Nagy, T.; Turányi, T. Uncertainty of Arrhenius parameters

Example: reaction $\text{O} + \text{N}_2\text{O} \rightarrow \text{NO} + \text{NO}$

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 $\text{O} + \text{N}_2\text{O} \rightarrow \text{NO} + \text{NO}$

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

\[ \sigma_K(\theta) = \sqrt{\theta^T \Sigma_p \theta} \]

For the 3-parameter Arrhenius equation:

\[ \sigma_K(\theta) = \sqrt{\sigma_\alpha^2 + \sigma_n^2 \ln^2 \theta + \sigma_e^2 \theta^{-2} + 2 r_{\alpha n} \sigma_\alpha \sigma_n \ln \theta - 2 r_{\alpha e} \sigma_\alpha \sigma_e \theta^{-1} - 2 r_{ne} \sigma_n \sigma_e \ln \theta \cdot \theta^{-1}} \]

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

\[ \sigma_\alpha, \sigma_n, \sigma_e, r_{\alpha e}, r_{n\alpha}, r_{ne} \]
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 written a MATLAB + Fortan code called \textit{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
   \textbf{source:} NIST Chemical Kientics Database + recent reviews

2. forward 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 \textit{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 $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$

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 $k^\text{min}$ and $k^\text{max}$ 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 are stored by the parameters of the covariance matrix

\[
\theta^T := \begin{bmatrix} 1 & \ln T & -T^{-1} \end{bmatrix} \quad \sigma_k(\theta) = \sqrt{\theta^T \Sigma_p \theta}
\]

T. Nagy, T. Turányi
Uncertainty of Arrhenius parameters
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 calculation of $f_{\text{prior}}(T)$ from

Programs called by `u-Limits`:

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

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

R1: \( \text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH} \)
R2: \( \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \) (low PL)
R3: \( \text{O} + \text{H}_2 \rightarrow \text{H} + \text{OH} \)
R4: \( \text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \)
R5: \( \text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2 + \text{HO}_2 \)
R6: \( \text{H} + \text{HO}_2 \rightarrow \text{OH} + \text{OH} \)
R7: \( \text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2 \)
R8: \( \text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2 \)
R9: \( \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \) (high PL)
R10: \( \text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M} \) (low PL)
R11: \( \text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M} \) (low PL)
R12: \( \text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M} \) (low PL)
R13: \( \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \)
R14: \( \text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{OH} \)
R15: \( \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \)
R16: \( \text{HCO} + \text{M} \rightarrow \text{H} + \text{CO} + \text{M} \)
R17: \( \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} \)
R18: \( \text{H} + \text{O} + \text{M} \rightarrow \text{OH} + \text{M} \) (low PL)
R19: \( \text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O} \)
R20: \( \text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO} \)
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 $f_{\text{prior}}(T)$ functions:

Parameters and model results

space of parameters

nominal parameter set of the model

model

nominal result of the model

space of model results
Uncertainty of model parameters

- Space of parameters
- Prior uncertainty domain of model parameters
- Model
- Space of model results
Uncertainty of model results

- Space of parameters
- Model
- Space of model results

Prior uncertainty domain of model parameters

Uncertainty domain of model results
Posterior uncertainty of parameters

- **space of parameters**
- **posterior uncertainty domain of model parameters**
- **model**
- **space of model results**
- **uncertainty domain of indirect experimental data**
Posterior uncertainty of parameters

- Space of parameters
- Posterior uncertainty domain of model parameters
- Model
- Space of model results
- 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 with 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

Determination of rate parameters based on both direct and indirect measurements.
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
- H₂/CO ratio 0.1 – 3.0

Initial mechanism –

C/H/O reactions of the Kéromnès et al. mechanism


Our recently published optimised hydrogen combustion mechanism


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, H₂, O₂, H₂O, CO, CO₂

<table>
<thead>
<tr>
<th>CO + OH = CO₂ + H</th>
<th>H + O₂ = O + OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + O₂ = CO₂ + O</td>
<td>H + O₂ + M = HO₂ + M</td>
</tr>
<tr>
<td>CO + HO₂ = CO₂ + OH</td>
<td>O + H₂ = H + OH</td>
</tr>
<tr>
<td>HCO + M = H + CO + M</td>
<td>HO₂ + H = OH + OH</td>
</tr>
<tr>
<td>HCO + H = CO + H₂</td>
<td>HO₂ + OH = H₂O + O₂</td>
</tr>
<tr>
<td>OH + OH = O + H₂O</td>
<td>H + OH + M = H₂O + M</td>
</tr>
<tr>
<td>H + H + M = H₂ + M</td>
<td>H + HO₂ = H₂ + O₂</td>
</tr>
<tr>
<td></td>
<td>OH + H₂ = H + H₂O</td>
</tr>
<tr>
<td></td>
<td>H₂O₂ + H = H₂ + HO₂</td>
</tr>
<tr>
<td></td>
<td>OH + OH + M = H₂O₂ + M</td>
</tr>
<tr>
<td></td>
<td>HO₂ + HO₂ = H₂O₂ + O₂</td>
</tr>
</tbody>
</table>
Optimisation and uncertainty calculation

**Optimisation** - minimisation of this error function:

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

- \( Y_{ij} \): measured/calculated rate coefficient OR measured/calculated ignition time/flame velocity in data point \( j \) of data series \( i \)
- \( \sigma \): 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:**

\[
\Sigma_p = \left[ (J_o^T W \Sigma_Y^{-1} J_o)^{-1} J_o^T W \Sigma_Y^{-1} \right] (\Sigma_Y + \Sigma_\Delta) \left[ (J_o^T W \Sigma_Y^{-1} J_o)^{-1} J_o^T W \Sigma_Y^{-1} \right]^T
\]
## The obtained rate parameters

<table>
<thead>
<tr>
<th>Optimized subset of reactions</th>
<th>Optimized parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\ln A$</td>
</tr>
<tr>
<td>R24 CO + OH = CO$_2$ + H</td>
<td>9.717</td>
</tr>
<tr>
<td>R1 H + O$_2$ = O + OH</td>
<td>36.16</td>
</tr>
<tr>
<td>R9 H + O$_2$ + M = HO$_2$ + M</td>
<td>45.41</td>
</tr>
<tr>
<td>R2 O + H$_2$ = H + OH</td>
<td>14.04</td>
</tr>
<tr>
<td>R11 HO$_2$ + H = OH + OH</td>
<td>31.69</td>
</tr>
<tr>
<td>R13 HO$_2$ + OH = H$_2$O + O$_2$</td>
<td>27.59</td>
</tr>
<tr>
<td>R8 H + OH + M = H$_2$O + M</td>
<td>55.66</td>
</tr>
<tr>
<td>R10 H + HO$_2$ = H$_2$ + O$_2$</td>
<td>14.57</td>
</tr>
<tr>
<td>R3 OH + H$_2$ = H + H$_2$O</td>
<td>16.40</td>
</tr>
<tr>
<td>R18 H$_2$O$_2$ + H = H$_2$ + HO$_2$</td>
<td>46.03</td>
</tr>
<tr>
<td>R16 OH + OH + M = H$_2$O$_2$ + M</td>
<td>42.14</td>
</tr>
<tr>
<td>R23 CO + O$_2$ = CO$_2$ + O</td>
<td>28.69</td>
</tr>
<tr>
<td>R25 CO + HO$_2$ = CO$_2$ + OH</td>
<td>16.53</td>
</tr>
<tr>
<td>R15 HO$_2$ + HO$_2$ = H$_2$O$_2$ + O$_2$</td>
<td>35.01</td>
</tr>
<tr>
<td>R26 HCO + M = H + CO + M</td>
<td>24.62</td>
</tr>
<tr>
<td>R28 HCO + H = CO + H$_2$</td>
<td>31.79</td>
</tr>
<tr>
<td>R4 OH + OH = O + H$_2$O</td>
<td>11.35</td>
</tr>
<tr>
<td>R5 H + H + M = H$_2$ + M</td>
<td>43.05</td>
</tr>
</tbody>
</table>

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.
Testing the optimised mechanism

- Laminar flame speed measurements of Santner et al. (2013)

Experiments:
Santner et al., *Proc. Combust. Inst.*, 34, 439-446 (2013)  \( T_0 = 295 \text{ K} \) equivalence ratio = 0.85 \( \text{H}_2:\text{CO} \) ratio = 1:1  5% steam added
Testing the optimised mechanism 2

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

Experiments:
## Comparison with other syngas mechanisms

### Syngas combustion

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Average error function</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IDT</td>
</tr>
<tr>
<td>ELTE Syngas 2016</td>
<td>14.83</td>
</tr>
<tr>
<td>NUIG NGM 2010</td>
<td>26.52</td>
</tr>
<tr>
<td>Kéromnès 2013</td>
<td>38.09</td>
</tr>
<tr>
<td>Davis 2005</td>
<td>52.04</td>
</tr>
<tr>
<td>POLIMI 2014</td>
<td>45.28</td>
</tr>
<tr>
<td>Li 2015 (PROCI)</td>
<td>19.80</td>
</tr>
<tr>
<td>Li 2007</td>
<td>50.77</td>
</tr>
<tr>
<td>USC 2007 II</td>
<td>64.17</td>
</tr>
<tr>
<td>San Diego 2014</td>
<td>30.38</td>
</tr>
<tr>
<td>Starik 2009</td>
<td>36.04</td>
</tr>
<tr>
<td>GRI 3.0 1999</td>
<td>77.23</td>
</tr>
<tr>
<td>Rasmussen 2008</td>
<td>87.12</td>
</tr>
<tr>
<td>Saxena Williams 2006</td>
<td>77.51</td>
</tr>
<tr>
<td>Sun 2007</td>
<td>133.69</td>
</tr>
<tr>
<td>No. of datasets</td>
<td>94</td>
</tr>
<tr>
<td>No. of data points</td>
<td>938</td>
</tr>
</tbody>
</table>
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: $f_{\text{original}} \rightarrow f_{\text{extreme}}$

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

- $\Sigma_p$ can be used to restore prior uncertainty parameter $f_{\text{prior}} (T)$

- $\Sigma_p$ 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

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

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

It is important for a practising 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.
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
Thank you for your attention!