Chemical Kinetic Optimization and Uncertainty Quantification

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Greetings to all women here!

Greetings on the International Women's Day!
The reaction mechanisms are getting larger, because
- increasing chemical knowledge
- faster computers with larger memory are available


Using detailed reaction mechanisms

This is a simplified 12-step hydrogen combustion mechanism:

1. $H_2 + O_2 \rightarrow H + HO_2$ $k_1(T)$
2. $H + O_2 \rightarrow OH + O$ $k_2(T)$
3. $OH + H_2 \rightarrow H + H_2O$ $k_3(T)$
4. $O + H_2 \rightarrow OH + H$ $k_4(T)$
5. $H + O_2 + M \rightarrow HO_2 + M$ $k_5(T, p)$
6. $H \rightarrow wall$ $k_6(T)$
7. $O \rightarrow wall$ $k_7(T)$
8. $OH \rightarrow wall$ $k_8(T)$
9. $HO_2 + H_2 \rightarrow H + H_2O_2$ $k_9(T)$
10. $2 \cdot HO_2 \rightarrow H_2O_2 + O_2$ $k_{10}(T)$
11. $H_2O_2 + M \rightarrow 2 \cdot OH + M$ $k_{11}(T, p)$
12. $HO_2 \rightarrow wall$ $k_{12}(T)$

Overall chemical equation: $2 \cdot H_2 + O_2 = H_2O$

Reality:

$H_2, O_2 \rightarrow H_2O$

Further parameters to each species: thermodynamical data, diffusion coefficients, viscosity

Temperature-dependence: 3-parameter Arrhenius-equation
Pressure-dependence: several more parameters
Predictive chemical kinetic models

Applications of chemical kinetic models:
- design of new equipment
- development of existing devices
- real-time control
- legislation (e.g. pollution control)

- automotive engines
- gas turbines (aerospace industry, power generation)
- manufacturing (e.g. CVD technology)
- chemical engineering

Parameters used:
- thermodynamics: enthalpies of formation, temperature dependence of $C_p$
- chemical kinetics: $k(T,p)$ of the reaction steps

Needed:
1) accurate values of the parameters
2) accurate estimation of the uncertainty of the parameters

Direct vs. indirect measurements in chemical kinetics

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

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

indirect measurements:
- simulation with a detailed mechanism is needed for the interpretation
- ignition delay times measured in shock tubes and RCMs
- laminar flame velocities
- exit concentrations in PSRs, final concentrations in shock tubes
- measured concentration–distance and/or concentration–time profiles in flames and tubular reactors
Uncertainty of reaction rate parameters

**Reaction rate parameters:**
Arrhenius parameters $A$, $n$, $E$,
$3^{rd}$ 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

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Prior uncertainty of rate coefficients

**space of rate parameters**

nominal parameter set of the kinetic model
Prior uncertainty of rate coefficients

space of rate parameters

prior uncertainty of the rate parameters from the direct measurements

Uncertainty of rate coefficients

uncertainty of a rate coefficient is defined via uncertainty parameter \( f \):

\[
f(T) = \log_{10}(k^0(T)/k^{\text{min}}(T)) = \log_{10}(k^{\text{max}}(T)/k^0(T))
\]

alternative: uncertainty factor \( u = 10^f \)

Uncertainty of a directly measured rate coefficient:

very high quality \( k \) uncertainty (3\( \sigma \)) factor of \( u = 1.3 \) \( (f = 0.1) \) \( \pm 8\% \) (1\( \sigma \))

good quality \( k \) uncertainty (3\( \sigma \)) factor of \( u = 2.0 \) \( (f = 0.3) \) \( \pm 26\% \) (1\( \sigma \))

typical \( k \) uncertainty (3\( \sigma \)) factor of \( u = 3.2 \) \( (f = 0.5) \) \( \pm 47\% \) (1\( \sigma \))
Uncertainty of Arrhenius parameters

The prior uncertainty domain of the Arrhenius parameters is needed

Original Arrhenius expression: \[ k(T) = A \exp(-E/RT) \]

Linearized form: \[ \ln\{k(T')\} = \ln\{A\} - (E/R)T^{-1} \]

Extended Arrhenius expression: \[ k(T) = AT^n \exp(-E/RT) \]

Linearized form: \[ \ln\{k(T')\} = \ln\{A\} + n \ln(T') - (E/R)T^{-1} \]

\[ \kappa = a + n \ln \theta - \epsilon \theta^{-1} \]

Domain of uncertainty of Arrhenius parameters

The simplest case: temperature independent uncertainty of \( k \)

Two Arrhenius parameters: \( \ln A, E/R \)
The simplest case: temperature independent uncertainty of $k$

two Arrhenius parameters $\ln A$, $E/R$

Domain of uncertainty of Arrhenius parameters

Chemical Kinetics Laboratory, Institute of Chemistry, Eötvös University (ELTE), Budapest, Hungary

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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 \( \ln A, E/R \)

![Diagram](image1)

3D domain of Arrhenius parameters

The most complex case: temperature dependent uncertainty of \( k \)
three Arrhenius parameters \( \alpha, \ln A, n, \varepsilon = E/R \)

![Diagram](image2)

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 \( \text{H}_2 \) and syngas combustion systems
Uncertainty of Arrhenius parameters

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

(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 prior uncertainty domain of the Arrhenius parameters is needed defined by the covariance matrix of the Arrhenius parameters

$\sigma(\ln k) \Rightarrow$ covariance matrix of the Arrhenius parameters

Matrix-vector form of the linearized Arrhenius equation:

$$\mathbf{p}^T := [a \ n \ \varepsilon]$$

$$\theta^T := [\ln \theta - \theta^{-1}]$$

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

$$\Sigma_p = (\mathbf{p} - \overline{\mathbf{p}})(\mathbf{p} - \overline{\mathbf{p}})^T = \begin{pmatrix}
\sigma_a^2 & \sigma_a \sigma_n & \sigma_a \sigma_{\varepsilon} \\
\sigma_n \sigma_a & \sigma_n^2 & \sigma_n \sigma_{\varepsilon} \\
\sigma_{\varepsilon} \sigma_a & \sigma_{\varepsilon} \sigma_n & \sigma_{\varepsilon}^2
\end{pmatrix}$$

$$\sigma_{\varepsilon}(\theta) = \sqrt{\theta^T \Sigma_p \theta}$$ equation for the conversion $\sigma(\ln k) \Leftrightarrow$ covariance matrix of the Arrhenius parameters

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

Parameters and simulation results

space of rate parameters

model

space of simulation results

nominal parameter set of the kinetic model

simulation result

Considering the uncertainties

space of rate parameters

model

space of simulation results

prior uncertainty of the rate parameters from the direct measurements

simulation result
Uncertainty of simulation results

Simulation uncertainty vs. indirect measurement uncertainty
Result of parameter optimisation

- **space of rate parameters**
- **model**
- **space of simulation results**

**posterior uncertainty**

of the rate parameters from the indirect measurements

**domain of uncertainty of the indirect measurements**

Mechanism optimisation

First suggestion for the systematic optimisation of a mechanism based on the low (projected) uncertainty of the indirect measurements:


The „GRI-Mech approach”:

- ✓ representative indirect experimental values are selected („targets”)
- ✓ parameters, highly sensitive with respect to the targets are identified („active parameters”)
- ✓ these active parameters are **A-factors**, 3rd body collision efficiencies and enthalpies of formation
- ✓ the fitting is assisted with surrogate models („response surfaces”)
- ✓ the fitted A-factors are limited by their uncertainty limits (calculated from uncertainty parameter $f$)
Further developments by Frenklach et al.

The objective function was extended:

it is penalized if the fitted $A$-factor deviates from the evaluated value
You, X.; Russi, T.; Packard, A.; Frenklach, M.

Extension of the methodology with the investigation of the consistency of the experimental data. See e.g.
Russi, T.; Packard, A.; Feeley, R.; Frenklach, M.

Encoding the indirect data using the PrIMe XML format:
Frenklach, M.
http://www.primekinetics.org/

Further developments by Sheen and Wang

The objective function was extended:
penalized if the fitted $A$ factor deviates from the evaluated value
D. Sheen, H. Wang:
Combust. Flame, 158, 645-656 (2011)

Calculation of the covariance matrix of the parameters ($A$-factors)
Method of Uncertainty Minimization using Polynomial Chaos Expansions (MUM-PCE)
D. Sheen, X. You, H. Wang, T. Løvås:

Fitting to original experimental datapoints
(not only fitting to selected targets)
Sheen, D.; Wang, H.
Combust. Flame, 158, 645-656 (2011)
Further developments by Cai and Pitsch

Optimization of rate rules for larger hydrocarbon models
⇒ less fitted parameters
⇒ consistency of rate coefficients of kinetically similar reactions

Our optimisation method

The aim is not only getting an optimised mechanism, but also the determination of the „real” values of the rate parameters and their joint domain of uncertainty.

Main features:
- original indirect experimental data are used (not „targets”)
- utilization of direct experimental data (instead of forcing $k$ to the evaluated value)
- all Arrhenius parameters ($A$, $n$, $E$) are fitted + 3rd body efficiencies (+ enthalpies of formation)
- determination of the prior uncertainty domain of the rate parameters based on direct measurements and theoretical calculations
- global optimisation within the prior uncertainty domain
- calculation of the joint posterior uncertainty of the fitted rate parameters from the experimental scatter of all (direct+indirect) experimental data
Selection of parameters to be fitted

Local sensitivity analysis is carried out at each experimental data point

The rate parameters having high sensitivity were selected for optimization (e.g. fitting)

Determination of the uncertainty range of the Arrhenius parameters

✓ based on direct measurements and theoretical calculations
✓ \( f(T) \) functions consistent with the mean Arrhenius expression are determined
✓ The shape and the prior pdf of the uncertainty domain of Arrhenius parameters are stored in their prior covariance matrix

Optimisation and uncertainty calculation

Optimisation = minimisation of this error function:

\[
E(p) = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{N_y} \sum_{j=1}^{N_y} \left( \frac{Y^\text{meas}(p) - Y^\text{exp}_y}{\sigma(Y^\text{exp}_y)} \right)^2
\]

\( Y_y \) measured/calculated rate coefficient OR measured/calculated ignition time/flame velocity in data point \( i \) of data series \( y \)
\( \sigma \) standard deviation of the measured data
\( N_y \) number of data points in data series \( y \)
\( N \) number of data series (different experiments)

Calculation of the covariance matrix of the estimated parameters:

\[
\Sigma_p = \left( J_o^T W \Sigma^{-1}_Y J_o \right)^{-1} \left( J_o^T W \Sigma^{-1}_Y \right)^T \left( \Sigma_Y + \Sigma_\Delta \right) \left( J_o^T W \Sigma^{-1}_Y J_o \right)^{-1} \left( J_o^T W \Sigma^{-1}_Y \right)^T
\]
Transformation of the covariance matrix to other measures of uncertainty

\[ \text{cov}(\kappa_i(T), \kappa_j(T)) = (\kappa_i(T) - \bar{\kappa}_i(T))(\kappa_j(T) - \bar{\kappa}_j(T)) = \Theta^T(p_i - \bar{p}_i)(p_j - \bar{p}_j)^T \Theta = \Theta^T \Sigma_{p_i,p_j} \Theta \]

\[ \sigma(\ln k) = \ln 10 \sigma(\log_{10} k) = \frac{\ln 10}{3} f(T) \]

Results of optimisation

• **Optimised detailed reaction mechanism**
  - Usually describes the experimental data much better

• **Set of optimised rate parameters**
  - All rate parameters are within the prior uncertainty domain

• **Posterior covariance matrix of the optimised parameters**
  - Temperature independent
  - ⇒ \( f(T) \) uncertainty function of each optimised rate coefficient
  - ⇒ correlation coefficients between pairs of rate coefficients

The same optimisation methodology can be used for
⇒ interpretation of indirect experimental data
⇒ development of detailed combustion mechanisms
Our publications related to the interpretation of experimental data

**Shock tube, H-ARAS concentration profiles**


Determination of rate parameters of cyclohexane and 1-hexene decomposition reactions


**Shock tube, H-ARAS and I-ARAS concentration profiles**

T. Varga, I. Gy. Zsély, T. Turányi, T. Bentz, M. Olzmann

Kinetic analysis of ethyl iodide pyrolysis based on shock tube measurements


**Shock tube, end product analysis**

V. Samu, T. Varga, K. Brezinsky, T. Turányi

Investigation of ethane pyrolysis and oxidation at high pressures using global optimization based on shock tube data


**Flow reactor, exit concentration measurements**

N. A. Buczkó, T. Varga, I. Gy. Zsély, T. Turányi

Formation of NO in N₂O₃/H₂O mixtures – re-evaluation of flow reactor experiments

*Fuel and Energy*, to be submitted

**Flame, NH₂ concentration profiles measured by ICLAS**

V. Samu, T. Varga, I. Rahinov, S. Chesiks, T. Turányi

Determination of rate parameters based on NH₂ concentration profiles measured in ammonia-doped methane–air flames,


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**Pyrolysis of ethyl-iodide**

Dr. Tobias Bentz and Prof. Matthias Olzmann (Karlsruhe Institute of Technology, Germany) investigated the decomposition of ethyl-iodide (C₂H₅I) in reflected shock wave experiments:

- 23 experiments with H-ARAS detection
- reflected shock wave experiments in Ar bath gas
- 6 experiments with I-ARAS detection

- Typical range of experiments:
  - \( T = 957 – 1530 \) K
  - \( p = 1.3 – 1.8 \) bar
  - \( c_0 = 2 – 5 \) ppm \( (2.1–6.6 \times 10^{13} \text{ cm}^{-3}) \)

- the results were described with a model of 5 reaction steps

Bentz, T., Szőri, M., Viskolcz, B., Olzmann, M.

Pyrolysis of ethyl iodide as hydrogen atom source: kinetics and mechanism in the temperature range 950–1200K

The initial mechanism

\[
\begin{align*}
\text{C}_2\text{H}_5\text{I} & \rightarrow \text{C}_2\text{H}_5 + \text{I} \quad \text{(R1)} \\
\text{C}_2\text{H}_5 + \text{M} & \rightarrow \text{C}_2\text{H}_4 + \text{H} + \text{M} \quad \text{(R2)} \\
\text{C}_2\text{H}_5\text{I} & \rightarrow \text{C}_2\text{H}_5 + \text{HI} \quad \text{(R3)} \\
\text{H} + \text{HI} & \rightarrow \text{H}_2 + \text{I} \quad \text{(R4)} \\
\text{C}_2\text{H}_5\text{I} + \text{H} & \rightarrow \text{C}_2\text{H}_5 + \text{HI} \quad \text{(R5)}
\end{align*}
\]

In the original mechanism of Bentz et al. the rate parameters of R1 were obtained by fitting to their H-ARAS measurement data, R3 and R5: TST calculations; R2 and R4: Baulch recommendations.

Sensitivity analysis considering the H-ARAS and I-ARAS concentration profiles indicated that the Arrhenius parameters of reactions R1, R3, R4, R5 can be determined from the measured H-atom and I-atom concentration profiles.

Utilization of external information

Our method allows the consideration of external information, like
- experimental data points measured in another laboratory
- published rate coefficient values measured at given \( T, p, \) bath gas.

In this work the measured rate coefficient values for reaction \( \text{H}_2 + \text{I} \rightarrow \text{H} + \text{HI} \) (-R4) were used from

Michael, J. V.; Kumaran, S.; Su, M. C.; Lim, K. P.  
13 rate coefficient values were measured using shock tube and light absorption detection.  
temperature range of 1755 – 2605 K

Vasileiadis S.; Benson S. W.  
1 measured rate coefficient  
\( T = 298 \text{ K} \)  
Very low pressure reactor, MS detection
Results of optimization

data used:
23  H–ARAS concentration profiles
6 I–ARAS concentration profiles
14 measurements for the rate coefficients of reaction \( \text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I} \) (R4)

The description of the experimental data improved significantly:

<table>
<thead>
<tr>
<th></th>
<th>original model</th>
<th>optimized model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total objective function value</td>
<td>5.07</td>
<td>3.57</td>
</tr>
<tr>
<td>Objective function value of the H-ARAS measurements</td>
<td>3.54</td>
<td>2.35</td>
</tr>
<tr>
<td>Objective function value of the I-ARAS measurements</td>
<td>1.17</td>
<td>1.14</td>
</tr>
<tr>
<td>Objective function value of the direct measurements</td>
<td>0.36</td>
<td>0.08</td>
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</table>

Optimized rate parameters

<table>
<thead>
<tr>
<th>reaction</th>
<th>initial model</th>
<th>optimized model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_5 + \text{I} )</td>
<td>( \log_{10}(A) ) 13.00, ( E/R ) 23200</td>
<td>( \log_{10}(A) ) 13.66, ( E/R ) 24422</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 \rightarrow \text{H} + \text{M} )</td>
<td>( \log_{10}(A) ) 18.00, ( E/R ) 16800</td>
<td>( \log_{10}(A) ) 18.00, ( E/R ) 16800</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI} )</td>
<td>( \log_{10}(A) ) 13.23, ( E/R ) 26680</td>
<td>( \log_{10}(A) ) 13.52, ( E/R ) 27110</td>
</tr>
<tr>
<td>( \text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I} )</td>
<td>( \log_{10}(A) ) 13.68, ( E/R ) 330</td>
<td>( \log_{10}(A) ) 13.82, ( E/R ) 492</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4\text{I} + \text{H} \rightarrow \text{C}_2\text{H}_5 + \text{HI} )</td>
<td>( \log_{10}(A) ) 15.62, ( E/R ) 3940</td>
<td>( \log_{10}(A) ) 15.00, ( E/R ) 2594</td>
</tr>
</tbody>
</table>
### Covariance matrix of the rate parameters

<table>
<thead>
<tr>
<th></th>
<th>( \ln A_1 )</th>
<th>( E_1/R )</th>
<th>( \ln A_2 )</th>
<th>( E_2/R )</th>
<th>( \ln A_3 )</th>
<th>( E_3/R )</th>
<th>( \ln A_4 )</th>
<th>( E_4/R )</th>
<th>( \ln A_5 )</th>
<th>( E_5/R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ln A_1 )</td>
<td>2.674E-02</td>
<td>4.072E+01</td>
<td>-8.606E-03</td>
<td>-2.127E+01</td>
<td>4.681E-03</td>
<td>1.182E+03</td>
<td>1.521E-01</td>
<td>3.578E+02</td>
<td>3.578E+02</td>
<td>3.578E+02</td>
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<tr>
<td>( E_1/R )</td>
<td>4.872E+00</td>
<td>9.679E-04</td>
<td>-9.214E-00</td>
<td>-2.270E+04</td>
<td>1.706E+00</td>
<td>3.860E+03</td>
<td>1.522E+02</td>
<td>3.587E+05</td>
<td>3.587E+05</td>
<td>3.587E+05</td>
</tr>
<tr>
<td>( \ln A_3 )</td>
<td>-8.606E-03</td>
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<td>7.153E-03</td>
<td>7.558E+00</td>
<td>-3.814E-03</td>
<td>-4.025E+00</td>
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<td>( E_3/R )</td>
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<tr>
<td>( \ln A_4 )</td>
<td>4.681E-03</td>
<td>1.706E+00</td>
<td>-3.814E-03</td>
<td>-1.009E+00</td>
<td>3.711E-03</td>
<td>1.750E+00</td>
<td>5.954E+01</td>
<td>6.017E+01</td>
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<td>( E_4/R )</td>
<td>1.182E-01</td>
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<td>7.558E+00</td>
<td>8.008E+03</td>
<td>-1.009E+00</td>
<td>3.711E-03</td>
<td>1.750E+00</td>
<td>5.954E-02</td>
<td>1.692E+01</td>
<td>1.692E+01</td>
</tr>
<tr>
<td>( \ln A_5 )</td>
<td>1.521E+01</td>
<td>1.522E+02</td>
<td>-1.035E+01</td>
<td>-1.105E+02</td>
<td>5.954E-02</td>
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<td>1.698E+00</td>
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<tr>
<td>( E_5/R )</td>
<td>3.578E+02</td>
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<td>1.707E+03</td>
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</tr>
</tbody>
</table>

### Posterior uncertainty parameters \( f(T) \)

**R1** \( \text{C}_2\text{H}_4\text{I} \rightarrow \text{C}_2\text{H}_5 + \text{I} \)

\[ f = 0.02 - 0.04 \Rightarrow \text{very well known} \]

**R3** \( \text{C}_2\text{H}_6\text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI} \)

\[ f = 0.10 - 0.25 \Rightarrow \text{well known} \]

**R4** \( \text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I} \)

\[ f = 0.06 - 0.07 \Rightarrow \text{very well known} \]

**R5** \( \text{C}_2\text{H}_6\text{I} + \text{H} \rightarrow \text{C}_2\text{H}_5 + \text{HI} \)

\[ f = 0.02 - 0.50 \Rightarrow \text{well known} \]

Only near 1000 K

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

**Reminder:**

\( f = 0.1 \Rightarrow \text{very well known} \); \( f = 0.3 \Rightarrow \text{well known} \); \( f = 0.5 \) typical good uncertainty
Correlation coefficients $r(T)$ between the rate coefficients

Strong correlation between the rate coefficients at all conditions

The correlation significantly changes with temperature

Branching ratio $k(R1)/(k(R1)+k(R3))$

$\text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_5 + \text{I} \ (R1)$ compared to $\text{C}_2\text{H}_5\text{I} \rightarrow$ products

Kumaran, Su, Lim, Michael

$\beta = 0.87 \pm 0.11$ in range 950 K – 2050 K

Yang and Tranter

$\beta > 0.87$ in range 1150 K – 1870 K

Miyoshi, Yamauchi, Kosaka, Koshi, Matsui

$\beta = 0.92 \pm 0.06$ in range 950 K – 1400 K.

Weber, Lemieux, Zhang

$\beta = 0.7 \pm 0.1$ in range 770 K – 1200 K.
Branching ratio $k(R1)/(k(R1)+k(R3))$

$C_2H_5I \rightarrow C_2H_5 + I \ (R1)$ compared to $C_2H_5I \rightarrow \text{products}$

Kumaran, Su, Lim, Michael
shock tube, H-ARAS and I-ARAS
$b = 0.87\pm 0.11$ in range 950 K – 2050 K

Yang and Tranter
incident shock wave,
laserschlieren (LS) densitometry
$b > 0.87$ in range 1150 K – 1870 K

Miyoshi, Yamauchi, Kosaka, Koshi, Matsui
shock tube, I-ARAS
$b = 0.92\pm 0.06$ in range 950 K – 1400 K.

Weber, Lemieux, Zhang
flash pyrolysis / VUV-SPI-TOFMS
$b = 0.7\pm 0.1$ in range 770 K – 1200 K
Branching ratio \( k(R1)/(k(R1)+k(R3)) \)

\[ \text{C}_2\text{H}_3\text{I} \rightarrow \text{C}_2\text{H}_5 + \text{I} \text{ (R1)} \] compared to \( \text{C}_2\text{H}_3\text{I} \rightarrow \text{products} \)

Kumaran, Su, Lim, Michael
shock tube, H-ARAS and I-ARAS
\( b = 0.87 \pm 0.11 \) in range 950 K – 2050 K

Yang and Tranter
incident shock wave,
laserschlieren (LS) densitometry
\( b > 0.87 \) in range 1150 K – 1870 K

Miyoshi, Yamauchi, Kosaka, Koshi, Matsui
shock tube, I-ARAS
\( b = 0.92 \pm 0.06 \) in range 950 K – 1400 K.

Weber, Lemieux, Zhang
flash pyrolysis / VUV-SPI-TOFMS
\( b = 0.7 \pm 0.1 \) in range 770 K – 1200 K
Detailed reaction mechanisms

Development of
detailed reaction mechanisms

Our publications related to the development of detailed reaction mechanisms

**Determination of the prior uncertainty of rate coefficients**
Uncertainty of the rate parameters of several important elementary reactions of the
H₂ and syngas combustion systems.

**Optimized hydrogen combustion mechanism**
Optimization of a hydrogen combustion mechanism using both direct and indirect measurements.

**Optimized syngas combustion mechanism**
Development of a joint hydrogen and syngas combustion mechanism based on an optimization approach

**Optimized ethanol combustion mechanism**
C. Olm, T. Varga, É. Valkó, S. Hartl, C. Hasse, T. Turányi
Development of an ethanol combustion mechanism based on a hierarchical optimization approach

**Optimized methanol combustion mechanism**
Uncertainty quantification of a newly optimized methanol and formaldehyde combustion mechanism
**Example:** optimization of a methanol and formaldehyde combustion mechanism

- **Methanol** is an alternative automotive fuel, fuel additive and feedstock in various industrial processes

- **Model system** for studies of C\textsubscript{1} combustion: important radicals include CH\textsubscript{2}OH and CH\textsubscript{3}O

- **Relevance** for the oxidation of higher hydrocarbons/oxygenates

- **Not all** experimentally observed combustion characteristics (e.g. ignition, flame propagation, speciation profiles) are well-described by available kinetic mechanisms

**Data collection of methanol combustion**

<table>
<thead>
<tr>
<th>Type of measurement</th>
<th>Data points</th>
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<tr>
<td>Ignition delay times</td>
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<td>Shock tube</td>
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<td>Shock tube (CH\textsubscript{2}O)</td>
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<td>Rapid compression machine</td>
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<td>Burning velocity measurements</td>
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<td>Outwardly/ spherically propagating flame</td>
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<td>Counterflow twin-flame</td>
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<td>Heat flux method / laminar flat flame</td>
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<td>Flame-cone method</td>
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<td>Rapid compression machine</td>
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<tr>
<td>Burning velocity measurements</td>
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<tr>
<td>Outwardly/ spherically propagating flame</td>
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<td>Counterflow twin-flame</td>
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<td>Flame-cone method</td>
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<tr>
<th>Concentration measurements</th>
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<td>Flow reactor concentration–time profiles</td>
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<td>Flow reactor conc.–time profiles (CH\textsubscript{2}O)</td>
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<td>Flow reactor outlet concentrations</td>
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<td>Flow reactor outlet concentrations (CH\textsubscript{2}O)</td>
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<td>Jet-stirred reactor outlet concentrations</td>
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<td>Shock tube concentration–time profiles</td>
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<td>Shock tube conc.–time profiles (CH\textsubscript{2}O)</td>
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<td>Flow reactor outlet concentrations (CH\textsubscript{2}O)</td>
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<td>Jet-stirred reactor outlet concentrations</td>
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<table>
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<tbody>
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<td>p / atm</td>
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<tr>
<td>T / K</td>
</tr>
</tbody>
</table>
Initial mechanism for optimization

**Starting point:** CH₃OH/CH₂O/CO mechanism of Li et al. (2007)

J. Li; Z. W. Zhao; A. Kazakov; M. Chaos; F. L. Dryer; J. J. Scire Jr.,

Update of rate coefficients in the H₂/CO sub-mechanism using values from our recently optimized joint hydrogen and syngas mechanism

Further modifications:

- Thermochemistry updated
- CH₃OH⁻H₂O₂ = CH₃O⁻H₂O₂
- OH₂O₂ abstraction channel added

**Local sensitivity analysis**

Important reactions in formaldehyde and methanol combustion

Brute force method (parameters varied by +5%) using the initial mechanism, shown: ([S]avg ≥ 0.1)

**Chemical Kinetics Laboratory, Institute of Chemistry, ELTE Eötvös Loránd University, Budapest, Hungary**
Mechanism optimization

- 57 Arrhenius parameters of 17 reactions optimized

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Arrhenius parameters</th>
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<tbody>
<tr>
<td>R14/R15</td>
<td>( \text{H}_2\text{O}_3 + \text{H}_2 \text{O} = \text{H}_2\text{O}_2 + \text{O}_2 )</td>
<td>0.30–0.70</td>
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<tr>
<td>R37 LPL</td>
<td>( \text{CH}_2\text{O} + \text{M} = \text{CO} + \text{H}_2 + \text{M} )</td>
<td>0.50</td>
</tr>
<tr>
<td>R38</td>
<td>( \text{CH}_2\text{O} + \text{H} = \text{HCO} + \text{H}_2 )</td>
<td>0.60</td>
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<tr>
<td>R40</td>
<td>( \text{CH}_2\text{O} + \text{OH} = \text{HCO} + \text{H}_2 )</td>
<td>0.34–0.43</td>
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<tr>
<td>R41</td>
<td>( \text{CH}_2\text{O} + \text{O}_2 = \text{HCO} + \text{O}_2 )</td>
<td>1.20</td>
</tr>
<tr>
<td>R47</td>
<td>( \text{CH}_2\text{H}_2 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH} )</td>
<td>0.46–0.76</td>
</tr>
<tr>
<td>R53</td>
<td>( \text{CH}_2\text{H}_2 + \text{O} = \text{CH}_2 + \text{O}_2 )</td>
<td>1.00</td>
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<tr>
<td>R60</td>
<td>( \text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{O}_2 )</td>
<td>0.50</td>
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<tr>
<td>R67 LPL</td>
<td>( \text{CH}_2\text{O} + \text{M} = \text{CH}_2\text{O} + \text{H} + \text{M} )</td>
<td>0.84–1.24</td>
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<tr>
<td>R77 HPL</td>
<td>( \text{OH} + \text{CH}_2 = \text{CH}_2\text{OH} )</td>
<td>0.34–0.84</td>
</tr>
<tr>
<td>R77 LPL</td>
<td>( \text{OH} + \text{CH}_3 + \text{M} = \text{CH}_2\text{OH} + \text{M} )</td>
<td>1.20</td>
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<tr>
<td>R80</td>
<td>( \text{CH}_2\text{OH} + \text{H} = \text{CH}_2\text{OH} + \text{H}_2 )</td>
<td>0.44–1.07</td>
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<tr>
<td>R81</td>
<td>( \text{CH}_2\text{OH} + \text{H} = \text{CH}_2\text{OH} + \text{H}_2 )</td>
<td>1.70</td>
</tr>
<tr>
<td>R83</td>
<td>( \text{CH}_2\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{H}_2 )</td>
<td>0.70</td>
</tr>
<tr>
<td>R84</td>
<td>( \text{CH}_2\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{H}_2 )</td>
<td>0.46–0.87</td>
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<tr>
<td>R85</td>
<td>( \text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2 )</td>
<td>0.80</td>
</tr>
<tr>
<td>R87</td>
<td>( \text{CH}_2\text{OH} + \text{H}_2 = \text{CH}_2\text{O} + \text{H}_2 )</td>
<td>1.10</td>
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<tr>
<td>R88</td>
<td>( \text{CH}_2\text{OH} + \text{H}_2 = \text{CH}_2\text{O} + \text{H}_2 )</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Temperature-dependent prior uncertainty limits from direct rate coefficient measurements and theoretical studies of the rate coefficient (method of Nagy et al.)


Mechanism optimization

- Optimization targets:
  - 517 Shock tube, 59 RCM ignition delay points
  - 153 Laminar burning velocity points
  - 2,508 Flow reactor species concentration points
  - 706 Jet-stirred reactor species concentration points
  - 20,460 Shock tube species concentration points
  - 926 Direct measurements of reaction rate coefficients
  - 33 Theoretical determinations of reaction rate coefficients

- Polynomial surrogate model ("response surfaces") used for computationally expensive flame simulations

- Hierarchical optimization strategy:
  Step-by-step inclusion of reactions and optimization targets
**Mechanism optimization results**

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$k_{\text{prior}}$</th>
<th>$k_{\text{posterior}}$</th>
<th>$k_{\text{prior}}/k_{\text{CO}}$</th>
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<tbody>
<tr>
<td>R14/R15</td>
<td>$\text{H}_2\text{O} + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$</td>
<td>0.30–0.70</td>
<td>0.08–0.71</td>
<td>0.09–0.57</td>
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<tr>
<td>R37 LPL</td>
<td>$\text{CH}_2\text{O} + \text{M} = \text{CO} + \text{H}_2\text{M}$</td>
<td>0.50</td>
<td>0.09–0.12</td>
<td>0.09–0.12</td>
</tr>
<tr>
<td>R38</td>
<td>$\text{CH}_2\text{O} + \text{H} + \text{H}_2\text{O}$</td>
<td>0.60</td>
<td>0.08–0.10</td>
<td>0.09–0.11</td>
</tr>
<tr>
<td>R40</td>
<td>$\text{CH}_2\text{O} + \text{OH} = \text{HCO} + \text{H}_2\text{O}$</td>
<td>0.34–0.43</td>
<td>0.22–0.30</td>
<td>0.19–0.27</td>
</tr>
<tr>
<td>R41</td>
<td>$\text{CH}_2\text{O} + \text{O} = \text{HCO} + \text{H}_2\text{O}$</td>
<td>1.20</td>
<td>0.19–0.20</td>
<td>0.18–0.20</td>
</tr>
<tr>
<td>R47</td>
<td>$\text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CH}_2\text{O} + \text{H}_2\text{O}$</td>
<td>0.46–0.76</td>
<td>0.26–0.49</td>
<td>0.26–0.38</td>
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<tr>
<td>R53</td>
<td>$\text{CH}_2\text{O} + \text{H}_2\text{O} = \text{H}_2\text{O} + \text{H}_2\text{O}_2$</td>
<td>1.00</td>
<td>0.25–0.45</td>
<td>0.25–0.32</td>
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<tr>
<td>R60</td>
<td>$\text{CH}_3\text{OH} + \text{O} = \text{CH}_2\text{O} + \text{H}_2\text{O}$</td>
<td>0.50</td>
<td>0.27–0.38</td>
<td>0.27–0.33</td>
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<tr>
<td>R67 LPL</td>
<td>$\text{CH}_3\text{O} + \text{CH}_2\text{O} + \text{H}_2\text{O}$</td>
<td>0.84–1.24</td>
<td>0.16–0.26</td>
<td>0.16–0.21</td>
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<td>R77 HPL</td>
<td>$\text{OH} + \text{CH}_2 = \text{CH}_2\text{OH}$</td>
<td>0.34–0.64</td>
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<td>R77 LPL</td>
<td>$\text{OH} + \text{CH}_2 + \text{M} = \text{CH}_2\text{OH} + \text{M}$</td>
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<td>$\text{CH}_2\text{O} + \text{H} + \text{H}_2\text{O}$</td>
<td>0.44–1.07</td>
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<td>R81</td>
<td>$\text{CH}_2\text{O} + \text{H}_2\text{O} + \text{H}_2\text{O}$</td>
<td>1.70</td>
<td>0.24–0.38</td>
<td>0.24–0.31</td>
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<td>R83</td>
<td>$\text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$</td>
<td>0.70</td>
<td>0.13–0.44</td>
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<td>R84</td>
<td>$\text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$</td>
<td>0.46–0.87</td>
<td>0.19–0.41</td>
<td>0.18–0.40</td>
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<td>R85</td>
<td>$\text{CH}_2\text{OH} + \text{O} = \text{CH}_2\text{O} + \text{H}_2\text{O}$</td>
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<td>0.78–1.01</td>
<td>0.72–0.91</td>
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<td>R87</td>
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<td>1.10</td>
<td>0.20–0.25</td>
<td>0.16–0.21</td>
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<td>R88</td>
<td>$\text{CH}_2\text{OH} + \text{H}_2\text{O} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$</td>
<td>0.70</td>
<td>0.15–0.42</td>
<td>0.15–0.26</td>
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When also considering all sensitive $\text{H}_2/\text{CO}$ reactions:

- $\text{R01}$: $\text{H}_2\text{O} + \text{O} = \text{HO}_2 + \text{H}$
- $\text{R03}$: $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$
- $\text{R08}$ LPL: $\text{H}_2\text{O} + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$
- $\text{R09}$ LPL: $\text{H}_2\text{O} + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$
- $\text{R10}$: $\text{H}_2\text{O} + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$
- $\text{R11}$: $\text{H}_2\text{O} + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$
- $\text{R13}$: $\text{H}_2\text{O} + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$
- $\text{R16}$ LPL: $\text{H}_2\text{O} + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$
- $\text{R24}$: $\text{CO} + \text{H} = \text{CO}_2 + \text{H}$
- $\text{R25}$: $\text{CO} + \text{H}_2 = \text{CO}_2 + \text{H}$
- $\text{R26}$ LPL: $\text{H}_2\text{O} + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$
- $\text{R28}$: $\text{H}_2\text{O} + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$
- $\text{R29}$: $\text{H}_2\text{O} + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$

and the corresponding $\text{H}_2/\text{CO}$ data.
Arrhenius plots (II)
Prior and posterior uncertainty ranges

Mechanism comparison results
Error function values for each type of data and overall

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<tr>
<th>Mechanism</th>
<th>Average error function value</th>
<th>Overall</th>
<th>No. of data sets</th>
<th>No. of data points</th>
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<td>Hamedane-2012</td>
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<td>Li-2007</td>
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<td>3.4</td>
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</tr>
<tr>
<td>Aramco1.3-2013</td>
<td>(41.3)</td>
<td>(11.1)</td>
<td>(178.4)</td>
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<td>NUQ-16.09-2016</td>
<td>(51.6)</td>
<td>(11.0)</td>
<td>(22.2)</td>
<td>(22.2)</td>
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<tr>
<td>Initial mechanism</td>
<td>8.1</td>
<td>2.3</td>
<td>74</td>
<td>475</td>
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<tr>
<td>Optimized mechanism</td>
<td>6.8</td>
<td>2.0</td>
<td>7</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>265</td>
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</tr>
</tbody>
</table>

**E** = $\frac{1}{N} \sum_{i=1}^{N} \frac{1}{N_i} \sum_{j=1}^{N_i} \left( \sigma \left( \frac{Y_i - \bar{Y}_i}{\sigma_Y} \right) \right)^2$

$E = 9$: data can be described within a 3σ uncertainty

**Improvement for all types of data!**

* Some RCM simulation results could not be obtained. Numbers shown are for the remaining data.

* Path profiles cannot be captured by the mechanism. Results shown do not include these profiles.

* Some simulation results could not be obtained or transport data were not available.
Result of parameter optimisation

- Space of rate parameters
- Model
- Space of simulation results
- Posterior uncertainty of the rate parameters
- Uncertainty of indirect measurement data calculated from the posterior uncertainty

Comparison of simulation results

- Propagation of rate coefficient posterior uncertainties
- Dots: measured flame velocity
- Simulated flame velocity
- Optimized mech
- Shading: pdf of the simulated flame velocity
- Optimized mech
- Simulated flame velocity using other mech’s
Summary

- **New optimized mechanism** for methanol and formaldehyde combustion simulations
- **Best reproduction** of indirect experimental data, while optimized rate coefficients are consistent with direct measurements and theoretical calculations within their uncertainty limits
- Determination of the **posterior uncertainty domain** of the rate parameters

ReSpecTh information web site

All computer codes for chemical kinetic optimisation and uncertainty quantification; all direct and indirect data files are freely available at web site [http://respecth.hu/](http://respecth.hu/)

Reaction kinetics, high-resolution molecular spectroscopy, and thermochemistry data
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