Chemical Kinetic Optimization and Uncertainty Quantification

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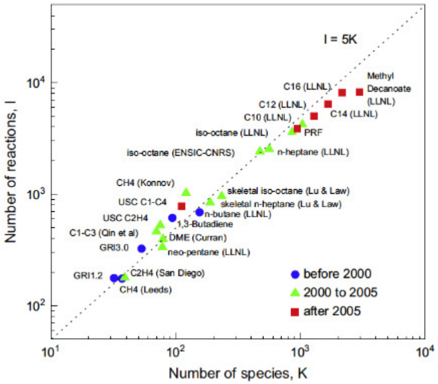
Greetings to all women here!

Greetings on the International Women's Day!

Using detailed reaction mechanisms

The reaction mechanisms are getting larger, because
– increasing chemical knowledge
– faster computers with larger memory are available



hydrogen combustion	30 reaction steps
natural gas combustion	300 reaction steps
petrol combustion	3000 reaction steps
Diesel oil combustion	15000 reaction steps

Lu T, Law CK: Toward accommodating realistic fuel chemistry in large-scale computations.
Prog. Energ. Combust. Sci.. **35**.192-215 (2009)

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	$2\ .HO_2 \rightarrow H_2O_2 + O_2$	$k_{10}(T)$
11	$H_2O_2 + M \rightarrow 2\ .OH + M$	$k_{11}(T, p)$
12	$.HO_2 \rightarrow$ wall	$k_{12}(T)$

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

reality:

$H_2, O_2 \rightarrow$
H_2, O_2 , H, O, OH, HO_2, H_2O_2
$\rightarrow H_2O$

k (*T*, *p*) temperature-dependence: 3-parameter Arrhenius-equation
pressure-dependence: several more parameters

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

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
- → 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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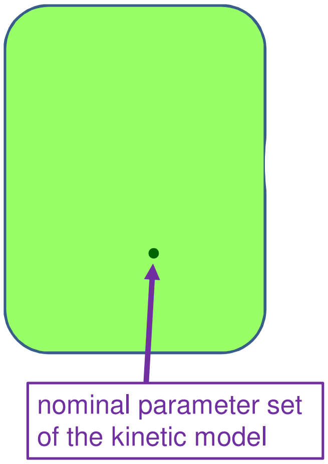
Prior uncertainty of rate coefficients

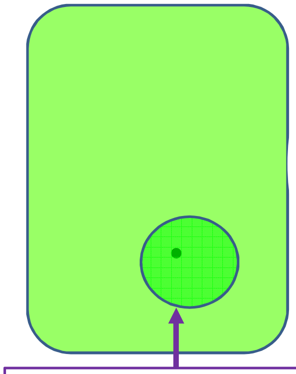
space of rate parameters



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* :

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

alternative: uncertainty factor $u=10^{f}$

Uncertainty of a directly measured rate coefficient:

very high quality *k* uncertainty (3σ) factor of *u*=1.3	(*f*=0.1)	±8 % (1σ)
good quality *k* uncertainty (3σ) factor of *u*=2.0	(*f*=0.3)	±26 % (1σ)
typical *k* uncertainty (3σ) factor of *u*=3.2	(*f*=0.5)	±47 % (1σ)

Uncertainty of Arrhenius parameters

the prior uncertainty domain of the Arrhenius parameters is needed

original Arrhenius expression: $\boldsymbol{k}(\boldsymbol{T}) = \boldsymbol{A}\exp(-E/RT)$

linearized form: $\ln\{k(T)\} = \ln\{A\} - (E/R)T^{-1}$

extended Arrhenius expression: $\boldsymbol{k}(\boldsymbol{T}) = \boldsymbol{A}\boldsymbol{T}^{\boldsymbol{n}}\exp(-E/RT)$

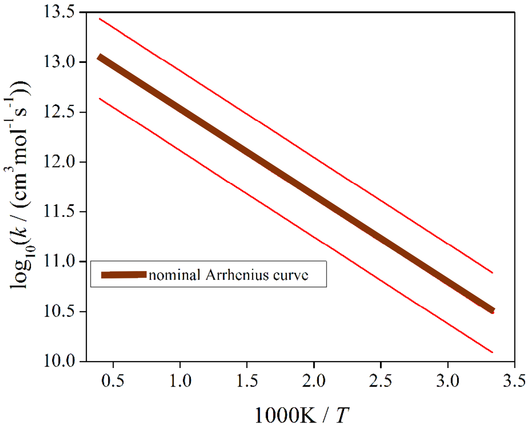
linearized form: $\ln\{k(T)\} = \ln\{A\} + n\,ln(T) - (E/R)T^{-1}$

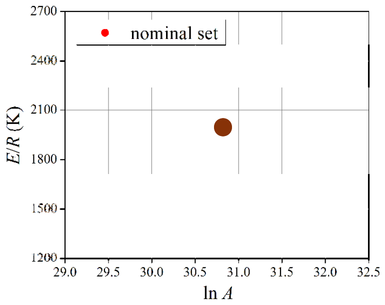
$$\kappa = \alpha + n\ln\theta - \epsilon\theta^{-1}$$

Domain of uncertainty of Arrhenius parameters

The simplest case: temperature independent uncertainty of *k*

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





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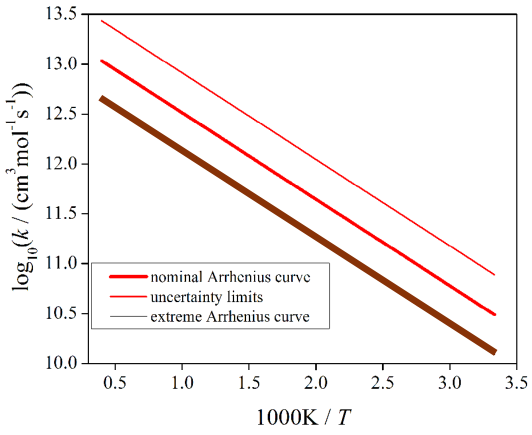

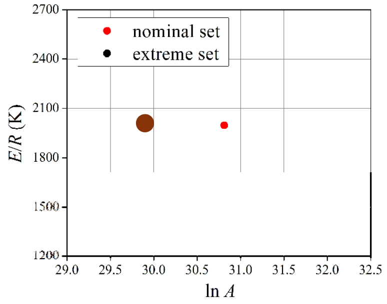

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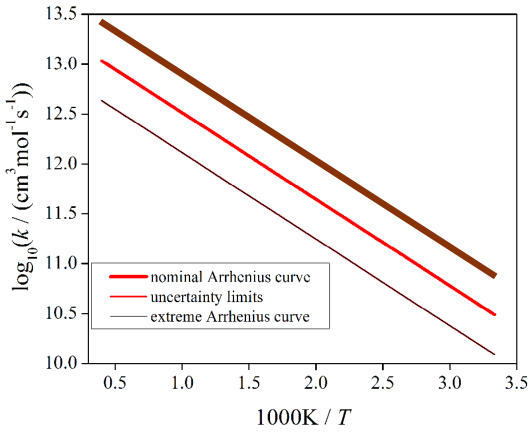

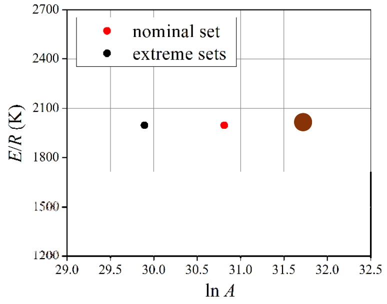

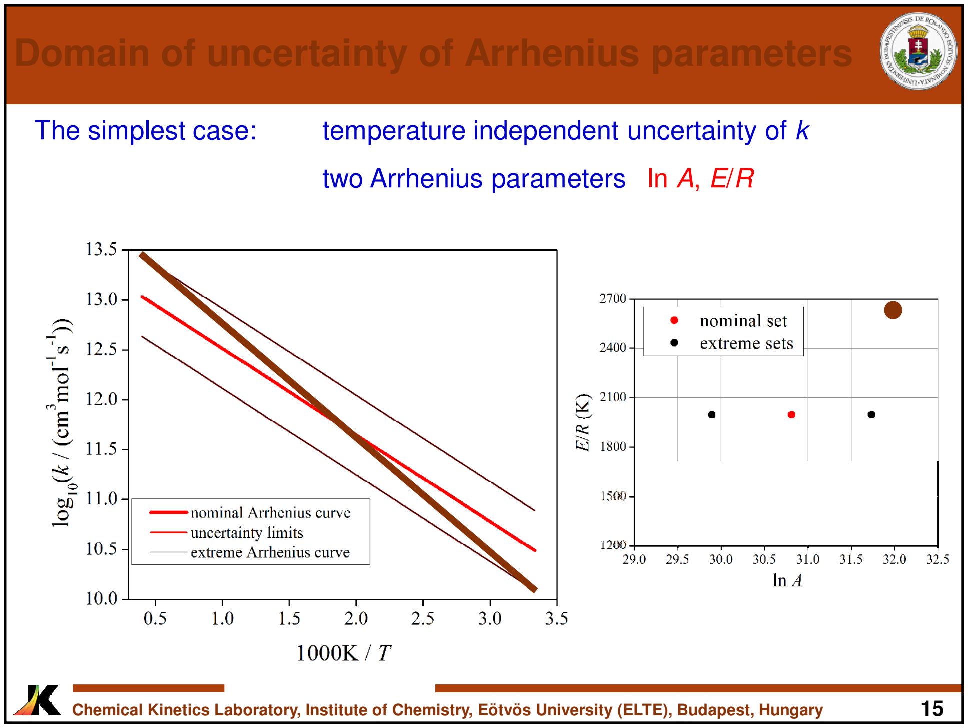

Domain of uncertainty of Arrhenius parameters

The simplest case: temperature independent uncertainty of *k*

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

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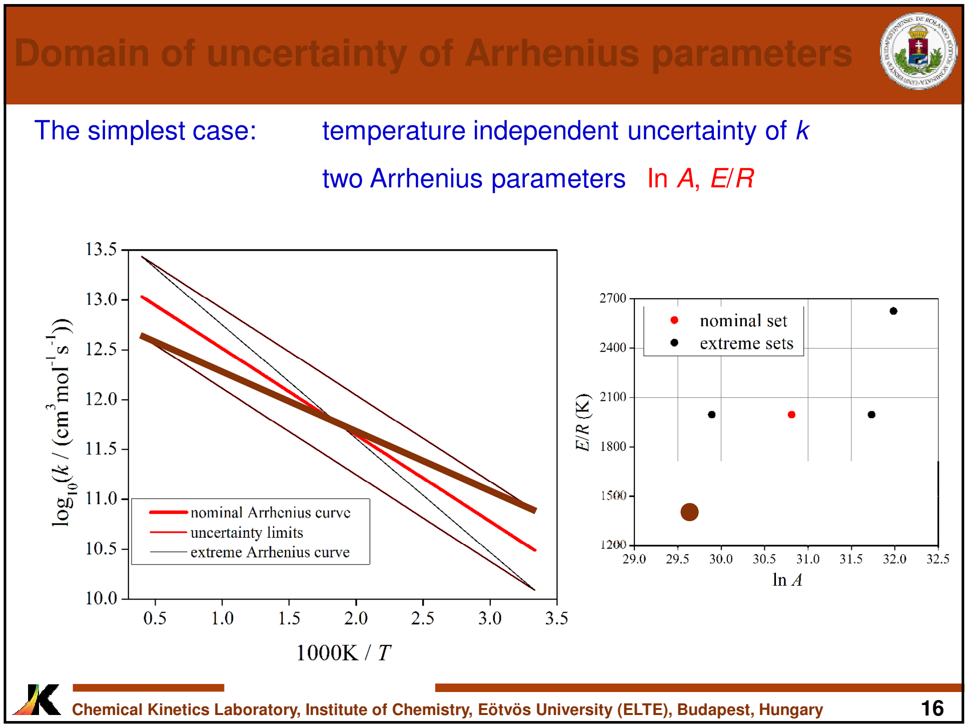

Domain of uncertainty of Arrhenius parameters

The simplest case: temperature independent uncertainty of *k*

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

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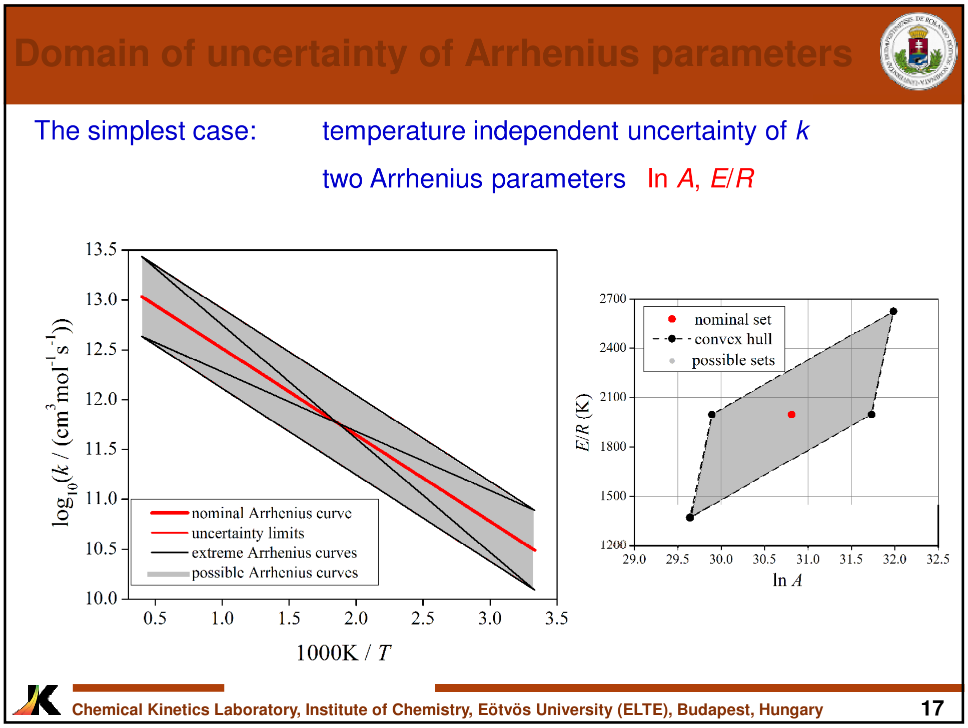
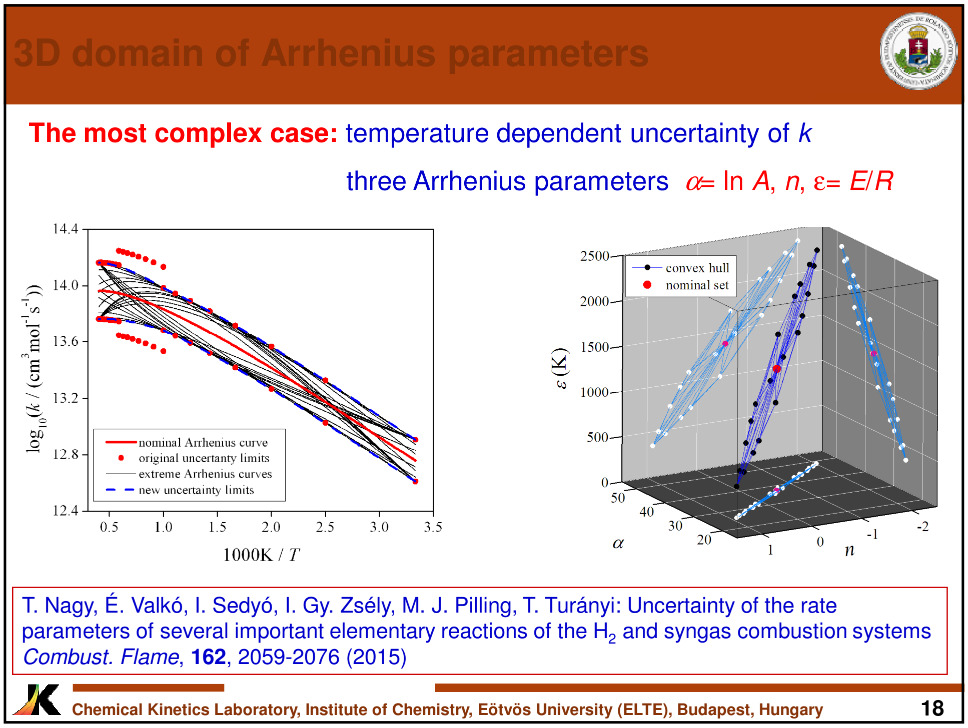


Domain of uncertainty of Arrhenius parameters

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*

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)

Uncertainty of Arrhenius parameters

Calculation of the variance of ln k from uncertainty parameter 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 prior uncertainty domain of the Arrhenius parameters is needed

defined by the covariance matrix of the Arrhenius parameters

σ(ln k) ⇒ covariance matrix of the Arrhenius parameters

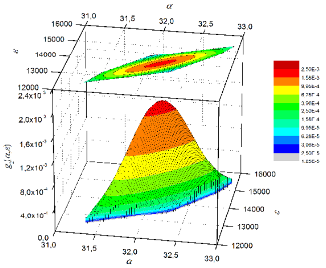
Matrix-vector form of the linearized Arrhenius equation:

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

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

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

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

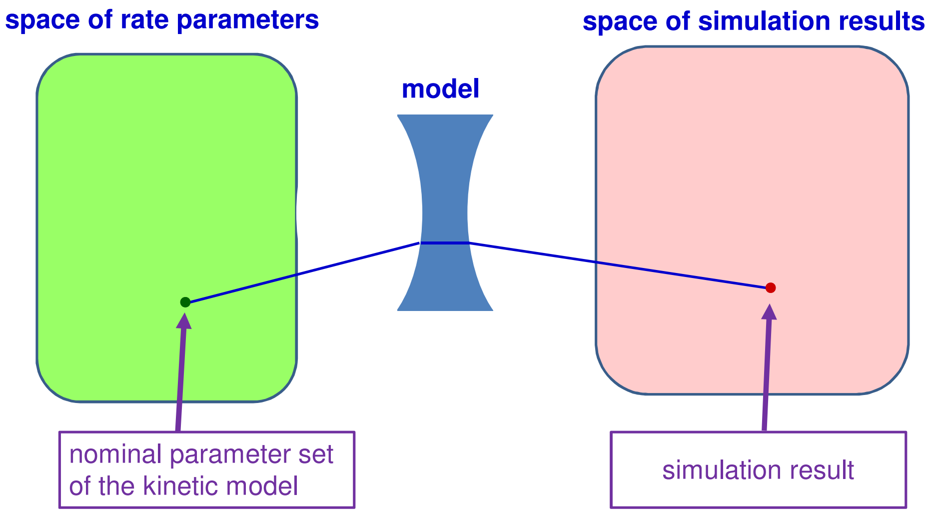


$$\boxed{\sigma_\kappa(\theta) = \sqrt{\boldsymbol{\theta}^{\mathrm{T}}\boldsymbol{\Sigma}_{\mathbf{p}}\boldsymbol{\theta}}}$$

equation for the conversion
σ(ln k) ⇔ covariance matrix of the Arrhenius parameters

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

Parameters and simulation results



space of rate parameters

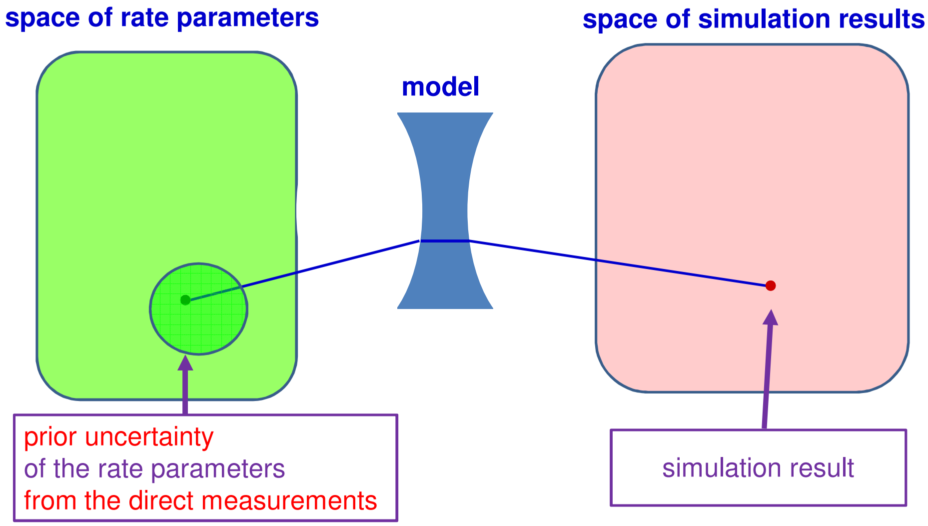
space of simulation results

model

nominal parameter set
of the kinetic model

simulation result

Considering the uncertainties



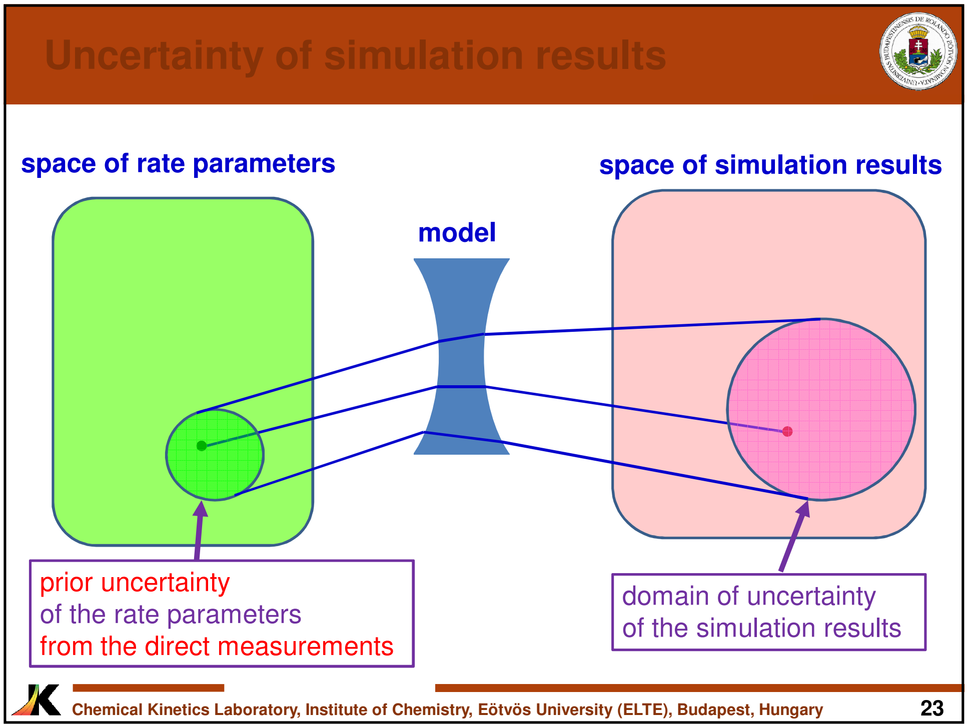
space of rate parameters

space of simulation results

model

prior uncertainty
of the rate parameters
from the direct measurements

simulation result



Uncertainty of simulation results

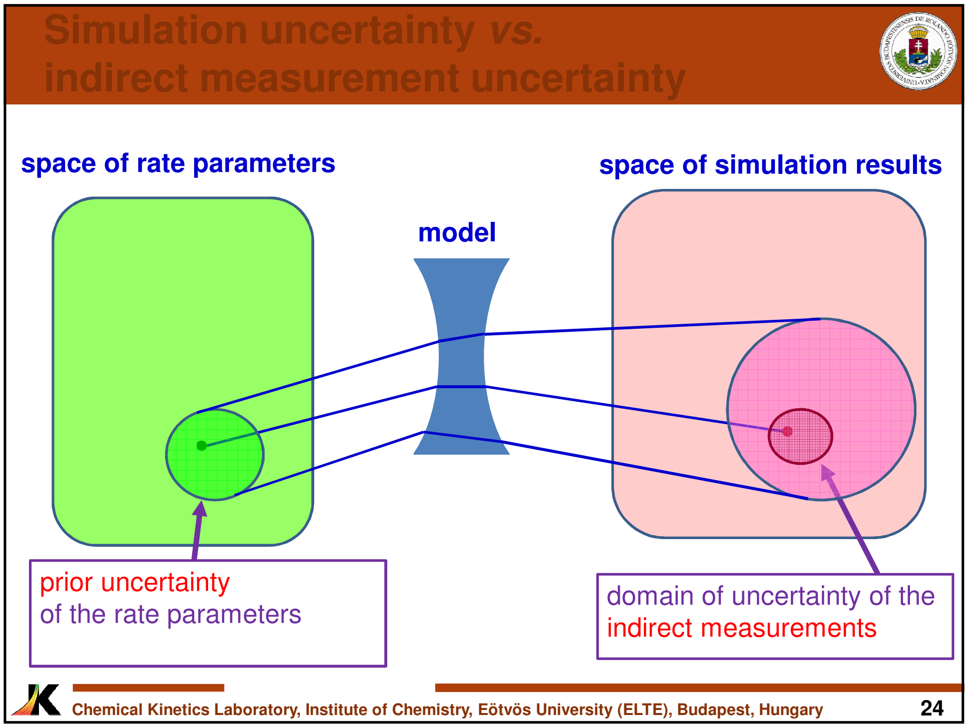
space of rate parameters

space of simulation results

model

prior uncertainty
of the rate parameters
from the direct measurements

domain of uncertainty
of the simulation results



Simulation uncertainty *vs.* indirect measurement uncertainty

space of rate parameters

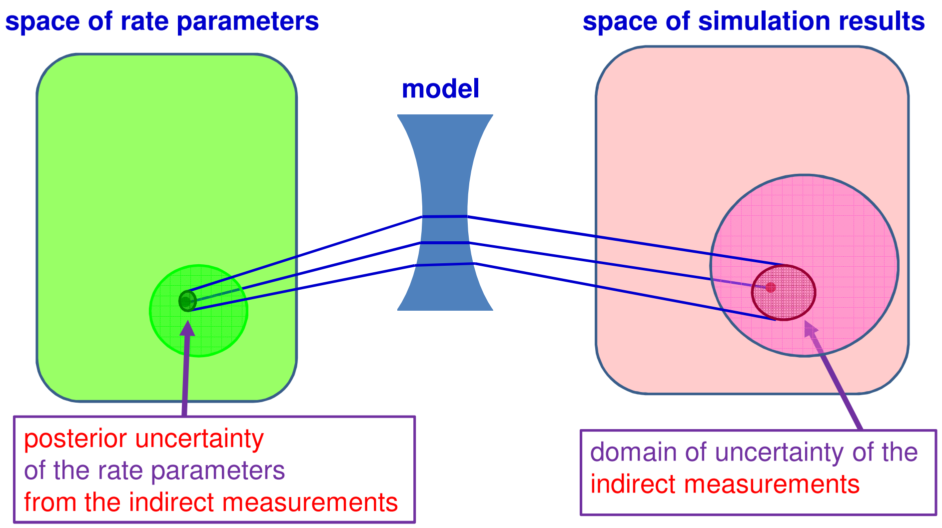
space of simulation results

model

prior uncertainty
of the rate parameters

domain of uncertainty of the
indirect measurements

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:

- Michael Frenklach, *Combust. Flame*, **58**, 69-72 (1984)
- M. Frenklach, H. Wang, M.J. Rabinowitz,
  Prog. Energy Combust. Sci., **18**, 47-73 (1992)

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.
Proc.Combust.Inst., **33**, 509-516 (2011)

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.
J. Phys. Chem. A, **112**, 2579-2588(2008)

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:
Proc. Combust. Inst., **32**, 535-542(2009).

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
L. M. Cai, H. Pitsch: *Combust. Flame* **161,** 405-415 (2014).

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

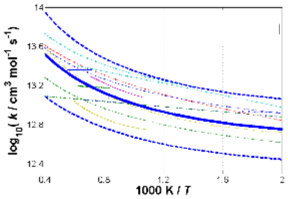
Selection of parameters to be fitted

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:

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

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

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

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:

$$\boxed{\mathbf{\Sigma_p} = \left[\left(\mathbf{J}_{\mathrm{o}}^{\mathrm{T}}\mathbf{W}\mathbf{\Sigma}_{\mathbf{Y}}^{-1}\mathbf{J}_{\mathrm{o}}\right)^{-1}\mathbf{J}_{\mathrm{o}}^{\mathrm{T}}\mathbf{W}\mathbf{\Sigma}_{\mathbf{Y}}^{-1}\right]\left(\mathbf{\Sigma}_{\mathbf{Y}} + \mathbf{\Sigma}_{\Delta}\right)\left[\left(\mathbf{J}_{\mathrm{o}}^{\mathrm{T}}\mathbf{W}\mathbf{\Sigma}_{\mathbf{Y}}^{-1}\mathbf{J}_{\mathrm{o}}\right)^{-1}\mathbf{J}_{\mathrm{o}}^{\mathrm{T}}\mathbf{W}\mathbf{\Sigma}_{\mathbf{Y}}^{-1}\right]^{\mathrm{T}}}$$

Transformation of the covariance matrix to other measures of uncertainty

covariance matrix of the Arrhenius parameters →
→ covariance matrix of ln *k* → *σ* (ln *k*) → uncertainty parameter *f*(*T*)

$$\mathrm{cov}\left(\kappa_i(T),\kappa_j(T)\right)=\overline{(\kappa_i(T)-\overline{\kappa}_i(T))(\kappa_j(T)-\overline{\kappa}_j(T))}=\Theta^T\overline{(p_i-\overline{p}_i)(p_j-\overline{p}_j)^T}\Theta=\Theta^T\Sigma_{p_i,p_j}\Theta$$

$$\boldsymbol{\theta}^T := \left[1 \quad \ln T \quad -T^{-1}\right]$$

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

covariance matrix of the Arrhenius parameters →
→ covariance matrix of ln *k* → correlation *r* (*T*) between ln k_i and ln k_j

$$r_{\kappa_i,\kappa_j}(T)=\frac{\mathrm{cov}\left(\kappa_i(T),\kappa_j(T)\right)}{\sigma_{\kappa_i}(T)\,\sigma_{\kappa_j}(T)}$$

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
I. Gy. Zsély, T. Varga, T. Nagy, M. Cserháti, T. Turányi, S. Peukert, M. Braun-Unkhoff, C. Naumann, U. Riedel
Determination of rate parameters of cyclohexane and 1-hexene decomposition reactions
Energy, **43**, 85-93(2012)

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
Int.J.Chem.Kinet., **46**, 295–304 (2014)

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
Proc. Combust. Inst., 36, 691–698 (2017)

Flow reactor, exit concentration measurements
N. A. Buczkó, T. Varga, I. Gy. Zsély, T. Turányi
Formation of NO in $N_2/O_2/H_2O$ mixtures – re-evaluation of flow reactor experiments
Fuel and Energy, to be submitted

Flame, NH_2 concentration profiles measured by ICLAS
V. Samu, T. Varga, I. Rahinov, S. Cheskis, T. Turányi
Determination of rate parameters based on NH_2 concentration profiles measured in ammonia-doped methane–air flames, *Fuel*, 212, 679-683 (2018)

Pyrolysis of ethyl-iodide

Dr. Tobias Bentz and Prof. Matthias Olzmann (Karlsruhe Institute of Technology, Germany) investigated the decomposition of ethyl-iodide (C_2H_5I) in reflected shock wave experiments:

Karlsruhe Institute of Technology

- 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 $\times 10^{13}$ 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
Zeitschrift für Physikalische Chemie **225,** 1117-1128 (2011)

The initial mechanism

$C_2H_5I \rightarrow C_2H_5 + I$ (R1)
$C_2H_5 + M \rightarrow C_2H_4 + H + M$ (R2)
$C_2H_5I \rightarrow C_2H_4 + HI$ (R3)
$H + HI \rightarrow H_2 + I$ (R4)
$C_2H_5I + H \rightarrow C_2H_5 + HI$ (R5)

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 $H_2 + I \rightarrow H + HI$ (-R4) were used from

Michael, J. V.; Kumaran, S.; Su, M. C.; Lim, K. P.
Chem. Phys. Lett. **319**, 99-106 (2000).
13 rate coefficient values were measured using shock tube and light absorption detection.
temperature range of 1755 – 2605 K

Vasileiadis S.; Benson S. W.
Int. J. Chem. Kinet. **29**, 915-925 (1997)
1 measured rate coefficient
$T = 298$ K
Very low pressure reactor, MS detection

Results of optimization

data used:

23 H–ARAS concentration profiles

6 I–ARAS concentration profiles

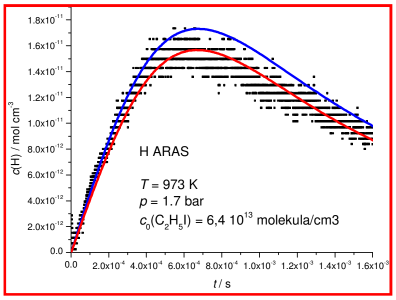
14 measurements for the rate coefficients of reaction H + HI => H_2 + I (R4)
(from Michael, Kumaran, Su, Lim: *Chem. Phys. Lett.* **319**, 99-106 (2000) and
Vasileiadis S.; Benson S. W.: *Int. J. Chem. Kinet.* **29**, 915-925 (1997))

The description of the experimental data improved significantly:

	original model	optimized model
Total objective function value	**5.07**	**3.57**
Objective function value of the H-ARAS measurements	3.54	2.35
Objective function value of the I-ARAS measurements	1.17	1.14
Objective function value of the direct measurements	0.36	0.08

Optimized rate parameters

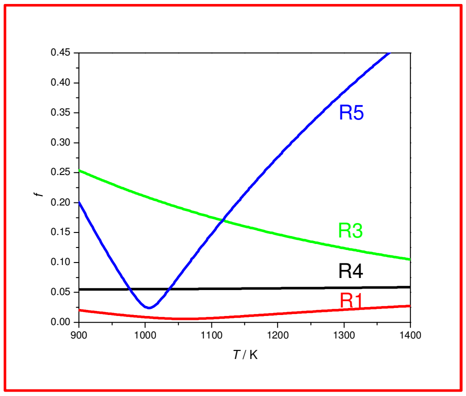
	initial model		optimized model	
	$\log_{10}(A)$	E/R	$\log_{10}(A)$	E/R
R1: $C_2H_5I \rightarrow C_2H_5 + I$	13.00	23200	13.66	24422
R2: $C_2H_5 + M \rightarrow C_2H_4 + H + M$	18.00	16800	18.00	16800
R3: $C_2H_5I \rightarrow C_2H_4 + HI$	13.23	26680	13.52	27110
R4: $H + HI \rightarrow H_2 + I$	13.68	330	13.82	492
R5: $C_2H_5I + H \rightarrow C_2H_5 + HI$	15.62	3940	15.00	2594



Covariance matrix of the rate parameters

	ln A_1	E_1/R	ln A_3	E_3/R	ln A_4	E_4/R	ln A_5	E_5/R
ln A_1	2.674E-02	4.872E+01	-8.606E-03	-2.127E+01	4.681E-03	1.182E+01	1.521E-01	3.578E+02
E_1/R	4.872E+01	9.679E+04	-9.214E+00	-2.270E+04	1.706E+00	3.860E+03	1.522E+02	3.587E+05
ln A_3	-8.606E-03	-9.214E+00	7.153E-03	7.558E+00	-3.814E-03	-4.025E+00	-1.035E-01	-1.041E+02
E_3/R	-2.127E+01	-2.270E+04	7.558E+00	8.008E+03	-1.009E+00	-1.100E+03	-1.105E+02	-1.112E+05
ln A_4	4.681E-03	1.706E+00	-3.814E-03	-1.009E+00	3.711E-03	1.750E+00	5.954E-02	6.017E+01
E_4/R	1.182E+01	3.860E+03	-4.025E+00	-1.100E+03	1.750E+00	1.595E+03	1.692E+01	1.682E+04
ln A_5	1.521E-01	1.522E+02	-1.035E-01	-1.105E+02	5.954E-02	1.692E+01	1.698E+00	1.707E+03
E_5/R	3.578E+02	3.587E+05	-1.041E+02	-1.112E+05	6.017E+01	1.682E+04	1.707E+03	1.717E+06

Posterior uncertainty parameters *f*(*T*)



R1 $C_2H_5I \rightarrow C_2H_5 + I$
f **= 0.02–0.04 ⇒ very well known**

R3 $C_2H_5I \rightarrow C_2H_4 + HI$
f **= 0.10–0.25 ⇒ well known**

R4 $H + HI \rightarrow H_2 + I$
f **= 0.06–0.07 ⇒ very well known**

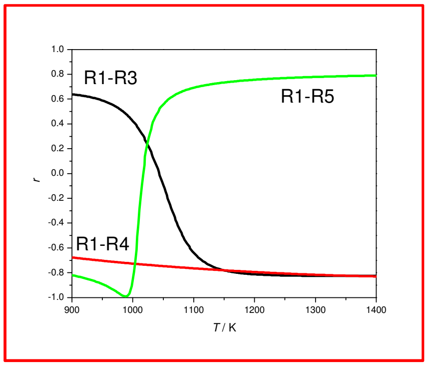
R5 $C_2H_5I + H \rightarrow C_2H_5 + HI$
f **= 0.02–0.50 ⇒ well known**
only near 1000 K

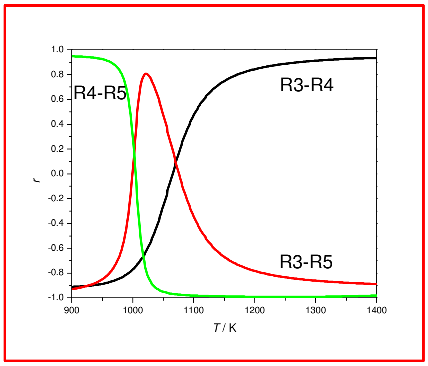
$$f(T)=\log_{10}\left(k^{0}(T)/k^{\min}(T)\right)=\log_{10}\left(k^{\max}(T)/k^{0}(T)\right)$$

Reminder:

f= 0.1 ⇒ very well known; *f*= 0.3 ⇒ well known; f= 0.5 typical good uncertainty

Correlation coefficients *r*(*T*) between the rate coefficients



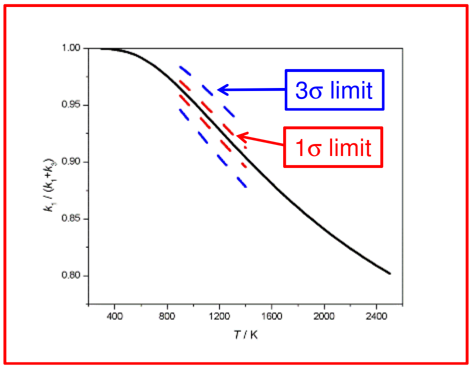


strong correlation between the rate coefficients at all conditions

the correlation significantly changes with temperature

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

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



Kumaran, Su, Lim, Michael
Proc. Combust. Inst. **26**, 605–611 (1996).
shock tube, H-ARAS and I-ARAS
b = 0.87±0.11 in range 950 K – 2050 K

Yang and Tranter
Int. J. Chem. Kinet. **44**, 433–443 (2012).
incident shock wave,
laserschlieren (LS) densitometry
b > 0.87 in range 1150 K – 1870 K

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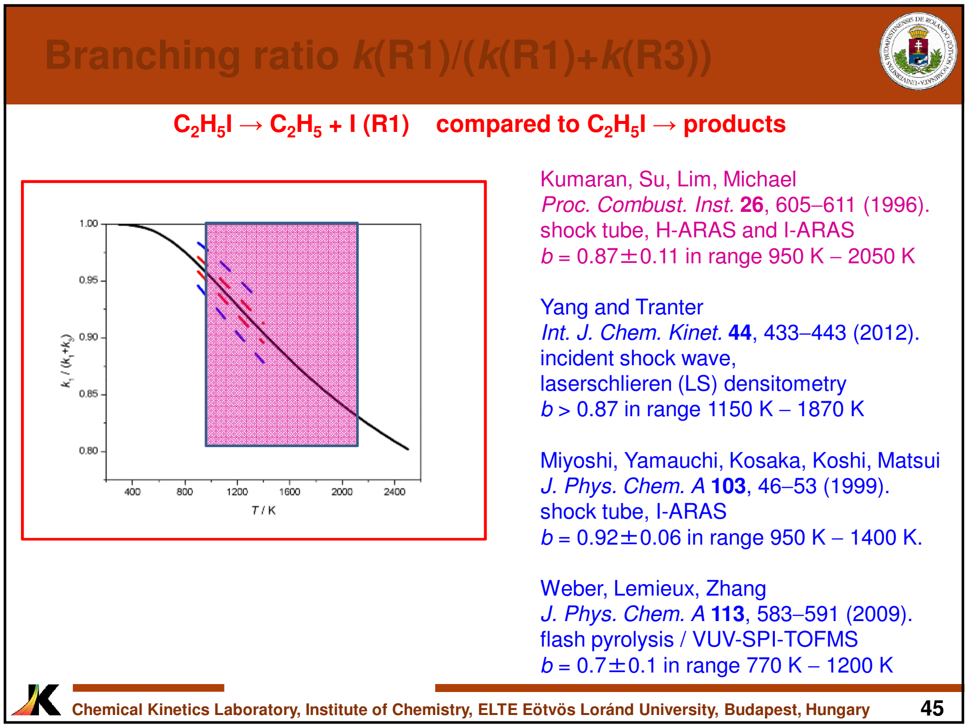
b = 0.7±0.1 in range 770 K – 1200 K



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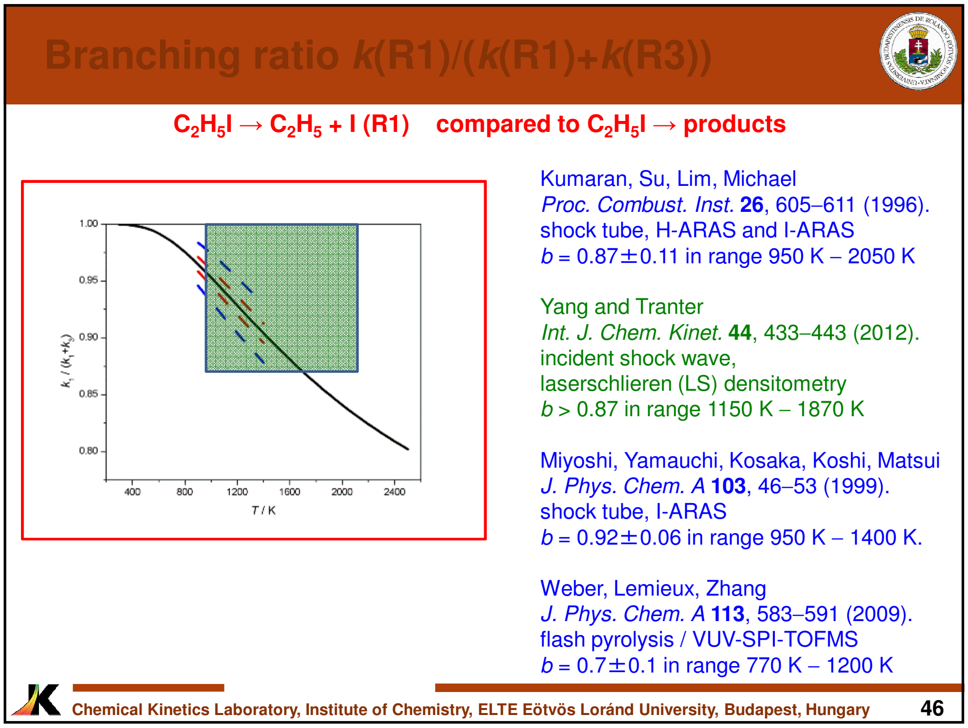

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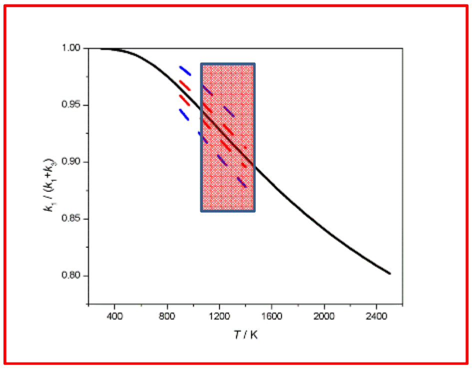

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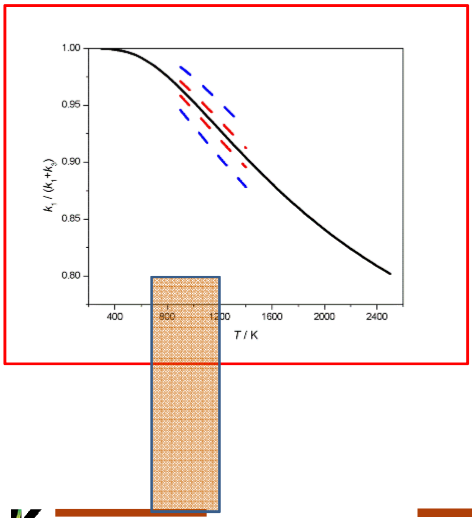

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Detailed reaction mechanisms

Development of

detailed reaction mechanisms

Our publications related to the development of detailed reaction mechanisms

Determination of the prior uncertainty of rate coefficients
T. Varga, 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)

Optimized 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
Optimization of a hydrogen combustion mechanism using both direct and indirect measurements
Proc. Combust. Inst., **35**, 589-596 (2015)

Optimized syngas combustion mechanism
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., **48**, 407–422 (2016)

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
Int.J.Chem.Kinet., **48**, 423–441 (2016)

Optimized methanol combustion mechanism
C. Olm, T. Varga, É. Valkó, H. J. Curran, T. Turányi
Uncertainty quantification of a newly optimized methanol and formaldehyde combustion mechanism
Combust. Flame, **186**, 45-64 (2017)

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_1 combustion**: important radicals include CH_2OH and CH_3O
- **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

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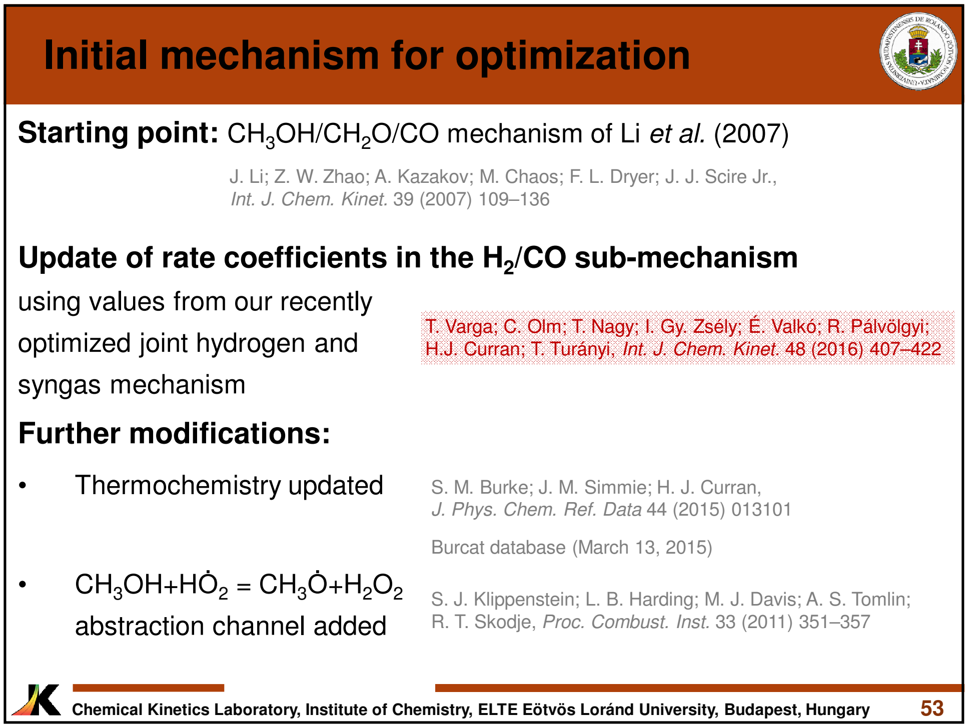
Data collection of methanol combustion

- **Indirect measurements**
- **Direct measure-ments** of rate coefficients
  (926 data points/ 66 data sets)
- **Theoretical rate determinations**
  (33 data sets)

Type of measurement experimental facility	**Data sets**	**Data points**	***p* / atm**	***T* / K**
Ignition delay times	**81**	**574**		
Shock tube	67	421	0.3–51.7	963–2180
Shock tube (CH_2O)	7	99	1.6	1363–2304
Rapid compression machine	7	54	9.3–40.6	817–980
Burning velocity measurements	**87**	**632**		
Outwardly/ spherically propagating flame	35	170	0.5–9.9	298–500
Counterflow twin-flame	5	90	1	298–368
Heat flux method / laminar flat flame	41	280	0.2–1	298–358
Flame-cone method	6	92	1	298–413
Concentration measurements	**97**	**23,694**		
Flow reactor concentration–time profiles	18	1,452	1–20	752–1043
Flow reactor conc.–time profiles (CH_2O)	13	462	1–6	852–1095
Flow reactor outlet concentrations	13	444	1–98.7	600–1443
Flow reactor outlet concentrations (CH_2O)	3	156	1.05	712–1279
Jet-stirred reactor outlet concentrations	9	711	1–20	697–1200
Shock tube concentration–time profiles	14	12,756	0.3–2.5	1266–2100
Shock tube conc.–time profiles (CH_2O)	27	7,713	1.5–2.0	1244–1907



Initial mechanism for optimization

Starting point: $CH_3OH/CH_2O/CO$ mechanism of Li *et al.* (2007)

J. Li; Z. W. Zhao; A. Kazakov; M. Chaos; F. L. Dryer; J. J. Scire Jr.,
Int. J. Chem. Kinet. 39 (2007) 109–136

Update of rate coefficients in the H_2/CO sub-mechanism

using values from our recently optimized joint hydrogen and syngas mechanism

T. Varga; C. Olm; T. Nagy; I. Gy. Zsély; É. Valkó; R. Pálvölgyi; H.J. Curran; T. Turányi, *Int. J. Chem. Kinet.* 48 (2016) 407–422

Further modifications:

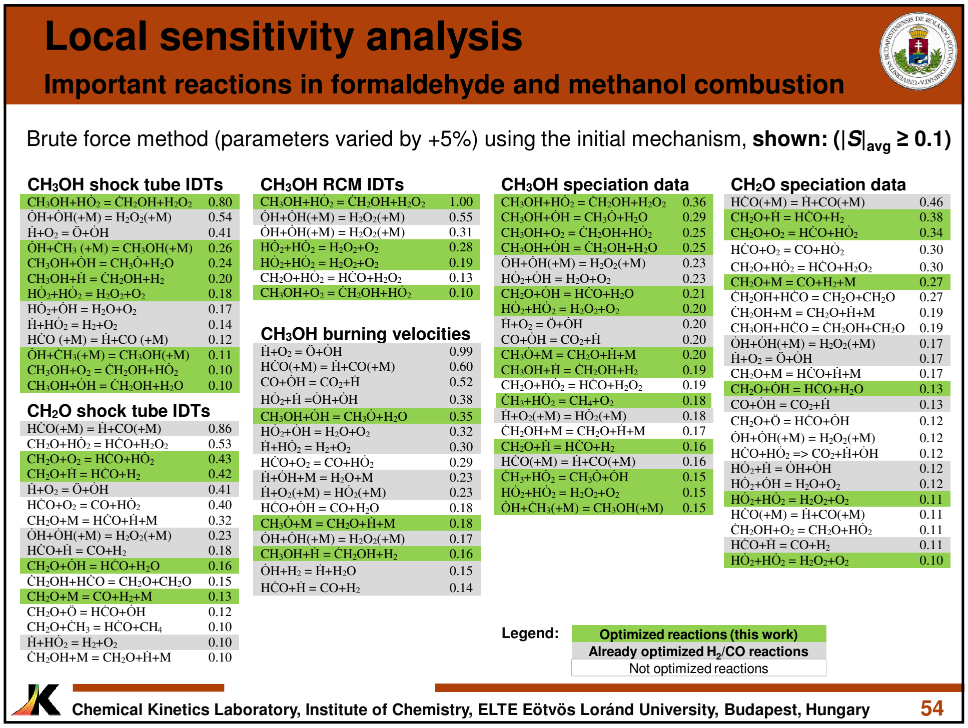
- Thermochemistry updated

S. M. Burke; J. M. Simmie; H. J. Curran,
J. Phys. Chem. Ref. Data 44 (2015) 013101

Burcat database (March 13, 2015)

- $CH_3OH+H\dot{O}_2 = CH_3\dot{O}+H_2O_2$ abstraction channel added

S. J. Klippenstein; L. B. Harding; M. J. Davis; A. S. Tomlin; R. T. Skodje, *Proc. Combust. Inst.* 33 (2011) 351–357



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)**

CH_3OH shock tube IDTs

🟩	$CH_3OH+H\dot{O}_2 = \dot{C}H_2OH+H_2O_2$	0.80
▨	$\dot{O}H+\dot{O}H(+M) = H_2O_2(+M)$	0.54
▨	$\dot{H}+O_2 = \ddot{O}+\dot{O}H$	0.41
🟩	$\dot{O}H+\dot{C}H_3\ (+M) = CH_3OH(+M)$	0.26
🟩	$CH_3OH+\dot{O}H = CH_3\dot{O}+H_2O$	0.24
🟩	$CH_3OH+\dot{H} = \dot{C}H_2OH+H_2$	0.20
🟩	$H\dot{O}_2+H\dot{O}_2 = H_2O_2+O_2$	0.18
▨	$H\dot{O}_2+\dot{O}H = H_2O+O_2$	0.17
▨	$\dot{H}+H\dot{O}_2 = H_2+O_2$	0.14
▨	$H\dot{C}O\ (+M) = \dot{H}+CO\ (+M)$	0.12
🟩	$\dot{O}H+\dot{C}H_3(+M) = CH_3OH(+M)$	0.11
🟩	$CH_3OH+O_2 = \dot{C}H_2OH+H\dot{O}_2$	0.10
🟩	$CH_3OH+\dot{O}H = \dot{C}H_2OH+H_2O$	0.10

CH_2O shock tube IDTs

▨	$H\dot{C}O(+M) = \dot{H}+CO(+M)$	0.86
⬜	$CH_2O+H\dot{O}_2 = H\dot{C}O+H_2O_2$	0.53
🟩	$CH_2O+O_2 = H\dot{C}O+H\dot{O}_2$	0.43
🟩	$CH_2O+\dot{H} = H\dot{C}O+H_2$	0.42
▨	$\dot{H}+O_2 = \ddot{O}+\dot{O}H$	0.41
⬜	$H\dot{C}O+O_2 = CO+H\dot{O}_2$	0.40
⬜	$CH_2O+M = H\dot{C}O+\dot{H}+M$	0.32
▨	$\dot{O}H+\dot{O}H(+M) = H_2O_2(+M)$	0.23
▨	$H\dot{C}O+\dot{H} = CO+H_2$	0.18
🟩	$CH_2O+\dot{O}H = H\dot{C}O+H_2O$	0.16
⬜	$\dot{C}H_2OH+H\dot{C}O = CH_2O+CH_2O$	0.15
🟩	$CH_2O+M = CO+H_2+M$	0.13
⬜	$CH_2O+\ddot{O} = H\dot{C}O+\dot{O}H$	0.12
⬜	$CH_2O+\dot{C}H_3 = H\dot{C}O+CH_4$	0.10
▨	$\dot{H}+H\dot{O}_2 = H_2+O_2$	0.10
⬜	$\dot{C}H_2OH+M = CH_2O+\dot{H}+M$	0.10

CH_3OH RCM IDTs

🟩	$CH_3OH+H\dot{O}_2 = \dot{C}H_2OH+H_2O_2$	1.00
▨	$\dot{O}H+\dot{O}H(+M) = H_2O_2(+M)$	0.55
⬜	$\dot{O}H+\dot{O}H(+M) = H_2O_2(+M)$	0.31
🟩	$H\dot{O}_2+H\dot{O}_2 = H_2O_2+O_2$	0.28
🟩	$H\dot{O}_2+H\dot{O}_2 = H_2O_2+O_2$	0.19
⬜	$CH_2O+H\dot{O}_2 = H\dot{C}O+H_2O_2$	0.13
🟩	$CH_3OH+O_2 = \dot{C}H_2OH+H\dot{O}_2$	0.10

CH_3OH burning velocities

▨	$\dot{H}+O_2 = \ddot{O}+\dot{O}H$	0.99
▨	$H\dot{C}O(+M) = \dot{H}+CO(+M)$	0.60
▨	$CO+\dot{O}H = CO_2+\dot{H}$	0.52
▨	$H\dot{O}_2+\dot{H} =\dot{O}H+\dot{O}H$	0.38
🟩	$CH_3OH+\dot{O}H = CH_3\dot{O}+H_2O$	0.35
▨	$H\dot{O}_2+\dot{O}H = H_2O+O_2$	0.32
▨	$\dot{H}+H\dot{O}_2 = H_2+O_2$	0.30
⬜	$H\dot{C}O+O_2 = CO+H\dot{O}_2$	0.29
▨	$\dot{H}+\dot{O}H+M = H_2O+M$	0.23
▨	$\dot{H}+O_2(+M) = H\dot{O}_2(+M)$	0.23
⬜	$H\dot{C}O+\dot{O}H = CO+H_2O$	0.18
🟩	$CH_3\dot{O}+M = CH_2O+\dot{H}+M$	0.18
▨	$\dot{O}H+\dot{O}H(+M) = H_2O_2(+M)$	0.17
🟩	$CH_3OH+\dot{H} = \dot{C}H_2OH+H_2$	0.16
▨	$\dot{O}H+H_2 = \dot{H}+H_2O$	0.15
▨	$H\dot{C}O+\dot{H} = CO+H_2$	0.14

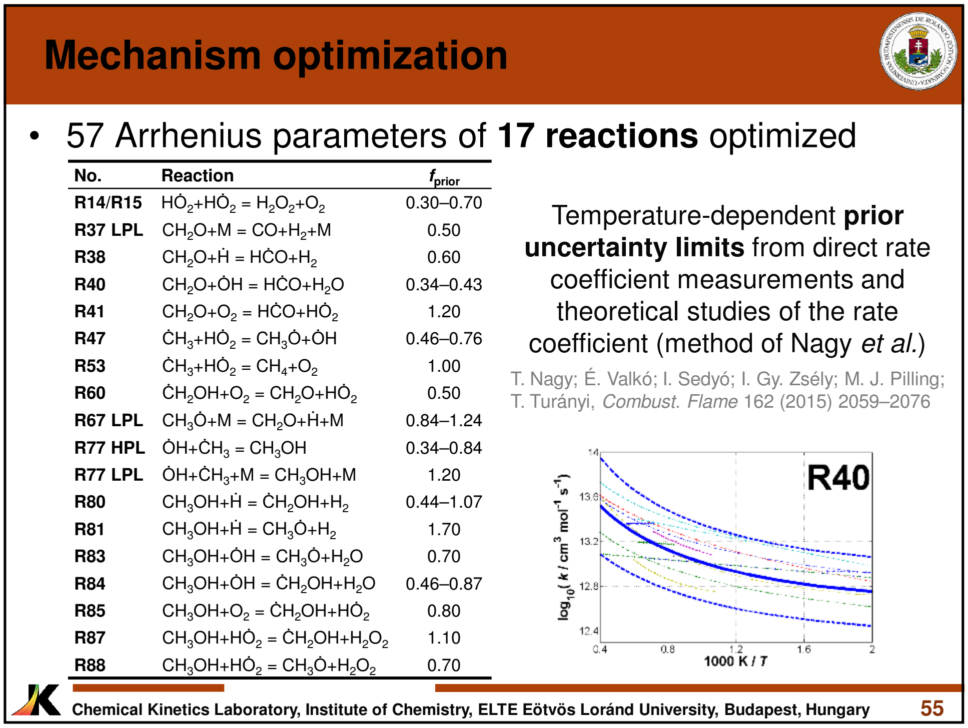
CH_3OH speciation data

🟩	$CH_3OH+H\dot{O}_2 = \dot{C}H_2OH+H_2O_2$	0.36
🟩	$CH_3OH+\dot{O}H = CH_3\dot{O}+H_2O$	0.29
🟩	$CH_3OH+O_2 = \dot{C}H_2OH+H\dot{O}_2$	0.25
🟩	$CH_3OH+\dot{O}H = \dot{C}H_2OH+H_2O$	0.25
▨	$\dot{O}H+\dot{O}H(+M) = H_2O_2(+M)$	0.23
▨	$H\dot{O}_2+\dot{O}H = H_2O+O_2$	0.23
🟩	$CH_2O+\dot{O}H = H\dot{C}O+H_2O$	0.21
🟩	$H\dot{O}_2+H\dot{O}_2 = H_2O_2+O_2$	0.20
▨	$\dot{H}+O_2 = \ddot{O}+\dot{O}H$	0.20
▨	$CO+\dot{O}H = CO_2+\dot{H}$	0.20
🟩	$CH_3\dot{O}+M = CH_2O+\dot{H}+M$	0.20
🟩	$CH_3OH+\dot{H} = \dot{C}H_2OH+H_2$	0.19
⬜	$CH_2O+H\dot{O}_2 = H\dot{C}O+H_2O_2$	0.19
🟩	$\dot{C}H_3+H\dot{O}_2 = CH_4+O_2$	0.18
▨	$\dot{H}+O_2(+M) = H\dot{O}_2(+M)$	0.18
⬜	$\dot{C}H_2OH+M = CH_2O+\dot{H}+M$	0.17
🟩	$CH_2O+\dot{H} = H\dot{C}O+H_2$	0.16
▨	$H\dot{C}O(+M) = \dot{H}+CO(+M)$	0.16
🟩	$\dot{C}H_3+H\dot{O}_2 = CH_3\dot{O}+\dot{O}H$	0.15
🟩	$H\dot{O}_2+H\dot{O}_2 = H_2O_2+O_2$	0.15
🟩	$\dot{O}H+\dot{C}H_3(+M) = CH_3OH(+M)$	0.15

CH_2O speciation data

▨	$H\dot{C}O(+M) = \dot{H}+CO(+M)$	0.46
🟩	$CH_2O+\dot{H} = H\dot{C}O+H_2$	0.38
🟩	$CH_2O+O_2 = H\dot{C}O+H\dot{O}_2$	0.34
⬜	$H\dot{C}O+O_2 = CO+H\dot{O}_2$	0.30
⬜	$CH_2O+H\dot{O}_2 = H\dot{C}O+H_2O_2$	0.30
🟩	$CH_2O+M = CO+H_2+M$	0.27
⬜	$\dot{C}H_2OH+H\dot{C}O = CH_2O+CH_2O$	0.27
⬜	$\dot{C}H_2OH+M = CH_2O+\dot{H}+M$	0.19
⬜	$CH_3OH+H\dot{C}O = \dot{C}H_2OH+CH_2O$	0.19
▨	$\dot{O}H+\dot{O}H(+M) = H_2O_2(+M)$	0.17
▨	$\dot{H}+O_2 = \ddot{O}+\dot{O}H$	0.17
⬜	$CH_2O+M = H\dot{C}O+\dot{H}+M$	0.17
🟩	$CH_2O+\dot{O}H = H\dot{C}O+H_2O$	0.13
▨	$CO+\dot{O}H = CO_2+\dot{H}$	0.13
⬜	$CH_2O+\ddot{O} = H\dot{C}O+\dot{O}H$	0.12
⬜	$\dot{O}H+\dot{O}H(+M) = H_2O_2(+M)$	0.12
⬜	$H\dot{C}O+H\dot{O}_2 => CO_2+\dot{H}+\dot{O}H$	0.12
▨	$H\dot{O}_2+\dot{H} = \dot{O}H+\dot{O}H$	0.12
▨	$H\dot{O}_2+\dot{O}H = H_2O+O_2$	0.12
🟩	$H\dot{O}_2+H\dot{O}_2 = H_2O_2+O_2$	0.11
⬜	$H\dot{C}O(+M) = \dot{H}+CO(+M)$	0.11
⬜	$\dot{C}H_2OH+O_2 = CH_2O+H\dot{O}_2$	0.11
▨	$H\dot{C}O+\dot{H} = CO+H_2$	0.11
🟩	$H\dot{O}_2+H\dot{O}_2 = H_2O_2+O_2$	0.10

Legend:
🟩 **Optimized reactions (this work)**
▨ **Already optimized H_2/CO reactions**
⬜ Not optimized reactions



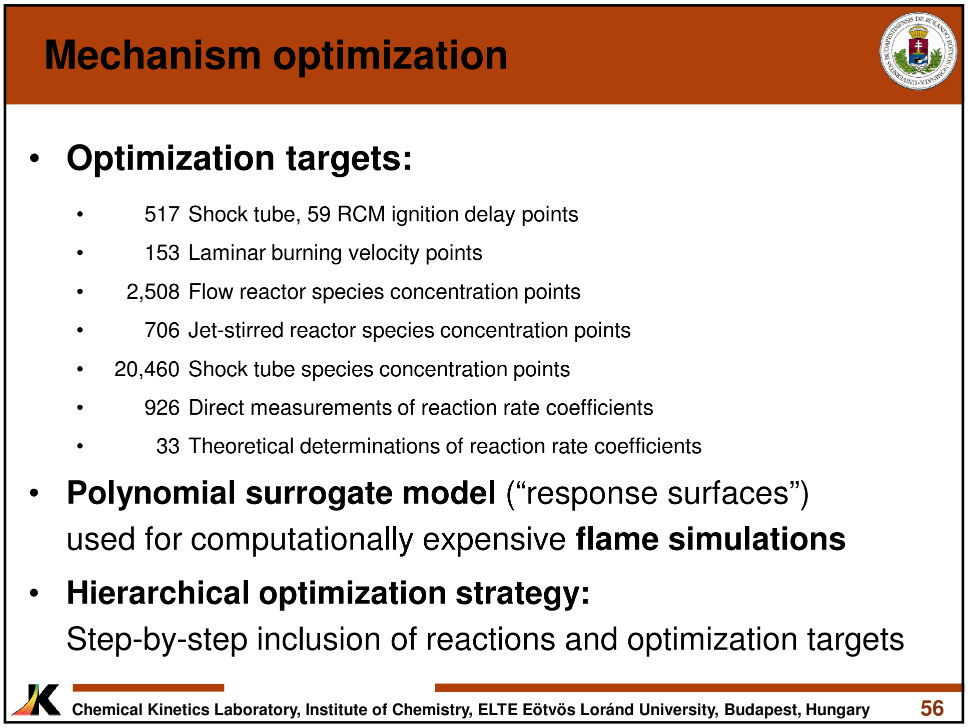
Mechanism optimization

- 57 Arrhenius parameters of **17 reactions** optimized

No.	**Reaction**	**f_{prior}**
R14/R15	$H\dot{O}_2+H\dot{O}_2 = H_2O_2+O_2$	0.30–0.70
R37 LPL	$CH_2O+M = CO+H_2+M$	0.50
R38	$CH_2O+\dot{H} = H\dot{C}O+H_2$	0.60
R40	$CH_2O+\dot{O}H = H\dot{C}O+H_2O$	0.34–0.43
R41	$CH_2O+O_2 = H\dot{C}O+H\dot{O}_2$	1.20
R47	$\dot{C}H_3+H\dot{O}_2 = CH_3\dot{O}+\dot{O}H$	0.46–0.76
R53	$\dot{C}H_3+H\dot{O}_2 = CH_4+O_2$	1.00
R60	$\dot{C}H_2OH+O_2 = CH_2O+H\dot{O}_2$	0.50
R67 LPL	$CH_3\dot{O}+M = CH_2O+\dot{H}+M$	0.84–1.24
R77 HPL	$\dot{O}H+\dot{C}H_3 = CH_3OH$	0.34–0.84
R77 LPL	$\dot{O}H+\dot{C}H_3+M = CH_3OH+M$	1.20
R80	$CH_3OH+\dot{H} = \dot{C}H_2OH+H_2$	0.44–1.07
R81	$CH_3OH+\dot{H} = CH_3\dot{O}+H_2$	1.70
R83	$CH_3OH+\dot{O}H = CH_3\dot{O}+H_2O$	0.70
R84	$CH_3OH+\dot{O}H = \dot{C}H_2OH+H_2O$	0.46–0.87
R85	$CH_3OH+O_2 = \dot{C}H_2OH+H\dot{O}_2$	0.80
R87	$CH_3OH+H\dot{O}_2 = \dot{C}H_2OH+H_2O_2$	1.10
R88	$CH_3OH+H\dot{O}_2 = CH_3\dot{O}+H_2O_2$	0.70

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

T. Nagy; É. Valkó; I. Sedyó; I. Gy. Zsély; M. J. Pilling; T. Turányi, *Combust. Flame* 162 (2015) 2059–2076



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

No.	Reaction	f_{prior}	$f_{posterior}$	$f_{posterior+H2/CO}$	
R14/R15	$H\dot{O}_2+H\dot{O}_2 = H_2O_2+O_2$	0.30–0.70	0.08–0.71	0.09–0.57	↘
R37 LPL	$CH_2O+M = CO+H_2+M$	0.50	0.09–0.12	0.09–0.12	→
R38	$CH_2O+\dot{H} = H\dot{C}O+H_2$	0.60	0.08–0.10	0.09–0.11	→
R40	$CH_2O+\dot{O}H = H\dot{C}O+H_2O$	0.34–0.43	0.22–0.30	0.19–0.27	↘
R41	$CH_2O+O_2 = H\dot{C}O+H\dot{O}_2$	1.20	0.19–0.20	0.18–0.20	→
R47	$\dot{C}H_3+H\dot{O}_2 = CH_3\dot{O}+\dot{O}H$	0.46–0.76	0.26–0.49	0.26–0.38	↘
R53	$\dot{C}H_3+H\dot{O}_2 = CH_4+O_2$	1.00	0.25–0.45	0.25–0.32	↘
R60	$\dot{C}H_2OH+O_2 = CH_2O+H\dot{O}_2$	0.50	0.27–0.38	0.27–0.33	↘
R67 LPL	$CH_3\dot{O}+M = CH_2O+\dot{H}+M$	0.84–1.24	0.16–0.26	0.16–0.21	→
R77 HPL	$\dot{O}H+\dot{C}H_3 = CH_3OH$	0.34–0.84	0.20–0.31	0.19–0.28	↘
R77 LPL	$\dot{O}H+\dot{C}H_3+M = CH_3OH+M$	1.20	0.07–0.39	0.07–0.27	↘
R80	$CH_3OH+\dot{H} = \dot{C}H_2OH+H_2$	0.44–1.07	0.18–0.27	0.17–0.24	→
R81	$CH_3OH+\dot{H} = CH_3\dot{O}+H_2$	1.70	0.24–0.38	0.24–0.31	→
R83	$CH_3OH+\dot{O}H = CH_3\dot{O}+H_2O$	0.70	0.13–0.44	0.12–0.25	↘
R84	$CH_3OH+\dot{O}H = \dot{C}H_2OH+H_2O$	0.46–0.87	0.19–0.41	0.18–0.40	→
R85	$CH_3OH+O_2 = \dot{C}H_2OH+H\dot{O}_2$	0.80	0.78–1.01	0.72–0.91	↘
R87	$CH_3OH+H\dot{O}_2 = \dot{C}H_2OH+H_2O_2$	1.10	0.20–0.25	0.16–0.21	↘
R88	$CH_3OH+H\dot{O}_2 = CH_3\dot{O}+H_2O_2$	0.70	0.15–0.42	0.15–0.26	↘

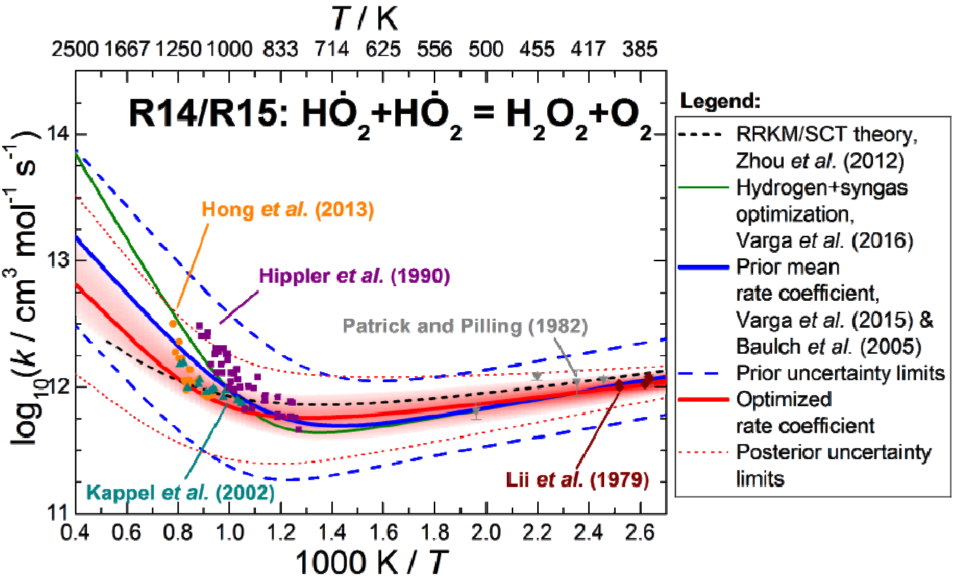
When also considering all sensitive H_2/CO reactions:

R01	$\dot{H}+O_2 = \ddot{O}+\dot{O}H$
R03	$\dot{O}H+H_2 = \dot{H}+H_2O$
R08 LPL	$\dot{H}+\dot{O}H+M = H_2O+M$
R09 LPL	$\dot{H}+O_2+M = H\dot{O}_2+M$
R10	$\dot{H}+H\dot{O}_2 = H_2+O_2$
R11	$H\dot{O}_2+\dot{H} = \dot{O}H+\dot{O}H$
R13	$H\dot{O}_2+\dot{O}H = H_2O+O_2$
R16 LPL	$\dot{O}H+\dot{O}H+M = H_2O_2+M$
24	$CO+\dot{O}H = CO_2+\dot{H}$
R25	$CO+H\dot{O}_2 = CO_2+\dot{O}H$
R26 LPL	$H\dot{C}O+M = \dot{H}+CO+M$
R28	$H\dot{C}O+H = CO+H_2$

and the corresponding H_2/CO data

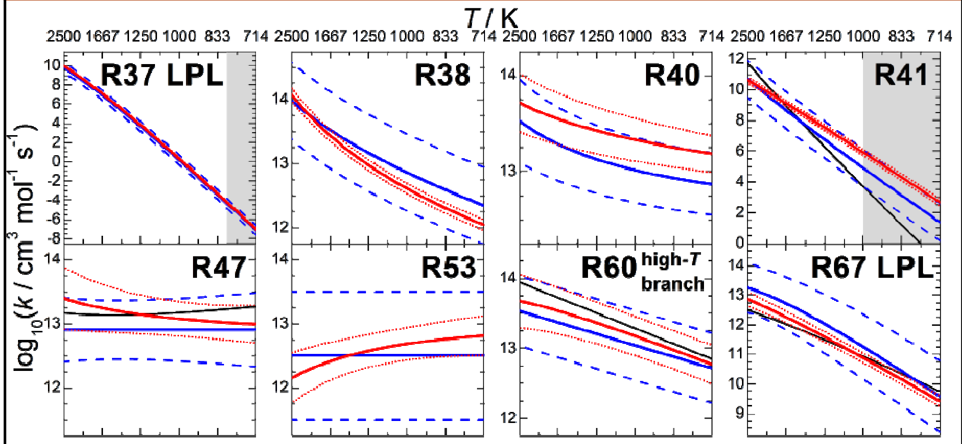
Arrhenius plots (I)

Prior and posterior uncertainty ranges



Arrhenius plots (II)

Prior and posterior uncertainty ranges



List of reactions:

R37 LPL	$CH_2O + M = CO + H_2 + M$	**R38**	$CH_2O + \dot{H} = H\dot{C}O + H_2$	**R40**	$CH_2O + \dot{O}H = H\dot{C}O + H_2O$	**R41**	$CH_2O + O_2 = H\dot{C}O + H\dot{O}_2$
R47	$\dot{C}H_3 + H\dot{O}_2 = CH_3\dot{O} + \dot{O}H$	**R53**	$\dot{C}H_3 + H\dot{O}_2 = CH_4 + O_2$	**R60**	$\dot{C}H_2OH + O_2 = CH_2O + H\dot{O}_2$	**R67 LPL**	$CH_3\dot{O} + M = CH_2O + \dot{H} + M$

Legend:

── Prior mean rate coefficient	── Optimized rate coefficient	── Li-2007 mechanism
- - Prior uncertainty limits	····· Posterior uncertaintylimits	*(if differing from ──)*

Mechanism comparison results

Error function values for each type of data and overall

Mechanism	Average error function value Ignition delay times CH₃OH	 Ignition delay times CH₂O	 Burning velocities CH₃OH	 Concentration profiles CH₃OH	 Concentration profiles CH₂O	**Overall**
AAU-2008	28.4	2.6	no transport	21.3	18.9	–
Alzueta-2001	103.9[a]	11.3	no transport	32.1	15.9	–
Christensen-2016	35.4	3.3	5.2	15.7	8.4	**16.3**
Hamdane-2012	41.2	6.4	(72.2)	109.6	12.9	**(59.8)**
Klippenstein-2011	131.8	3.4	1.7	14.9	6.4	**41.5**
Li-2007	7.6	3.4	1.9	14.8	6.4	**6.9**
Rasmussen-2008	32.2	5.2	17.9	40.9	12.3	**25.3**
CaltechMech2.3-2015	51.4	2.5	3.0	15.9	6.4	**19.7**
Johnson-2009	11.8	10.9	no transport	19.9	13.1	–
Kathrotia-2011	10.7	8.2	[3.0]	60.9	43.0	**[23.6]**
Konnov-2009	54.6	7.5	[76.0]	25.6[b]	37.2	**[51.7][b]**
Leplat-2011	410.5[a]	6.1	22.2	52.6	38.1	**131.6[a]**
Marinov-1999	260.7	20.7	(14.1)	36.7	30.4	**(90.4)**
SanDiego-2014	24.7	1.6	3.8	31.4	10.0	**16.2**
SaxenaWilliams-2007	86.2	1.7	2.3	17.3	9.6	**30.0**
USC-II-2007	602.8[a]	2.3	(8.5)	27.8	19.1	**(178.4)[a]**
Aramco1.3-2013	(41.3)	(11.1)	(4.3)	(16.0)	(12.7)	**(18.6)**
NUIG-16.09-2016	(51.6)	(11.0)	(4.2)	(20.0)	(12.4)	**(22.2)**
Initial mechanism	8.1	2.3	2.1	15.1	12.4	**8.1**
Optimized mechanism	6.8	2.0	1.6	12.0	6.3	**5.9**
No. of data sets	**74**	**7**	**87**	**54**	**43**	**265**
No. of data points	**475**	**99**	**632**	**15,363**	**8,331**	**24,900**

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

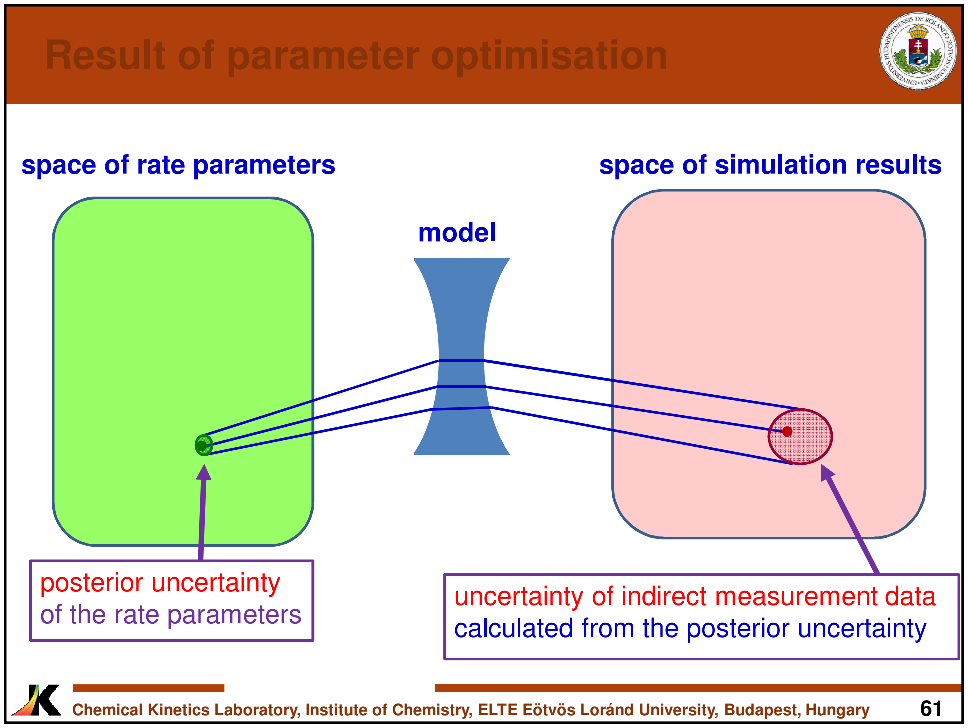
$E = 9$: data can be described within a 3σ uncertainty

Improvement for all types of data!

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

[b] CH_4 profiles cannot be captured by the mechanism. Results shown do not include those profiles

– Some simulation results could not be obtained or transport data were not available



Result of parameter optimisation

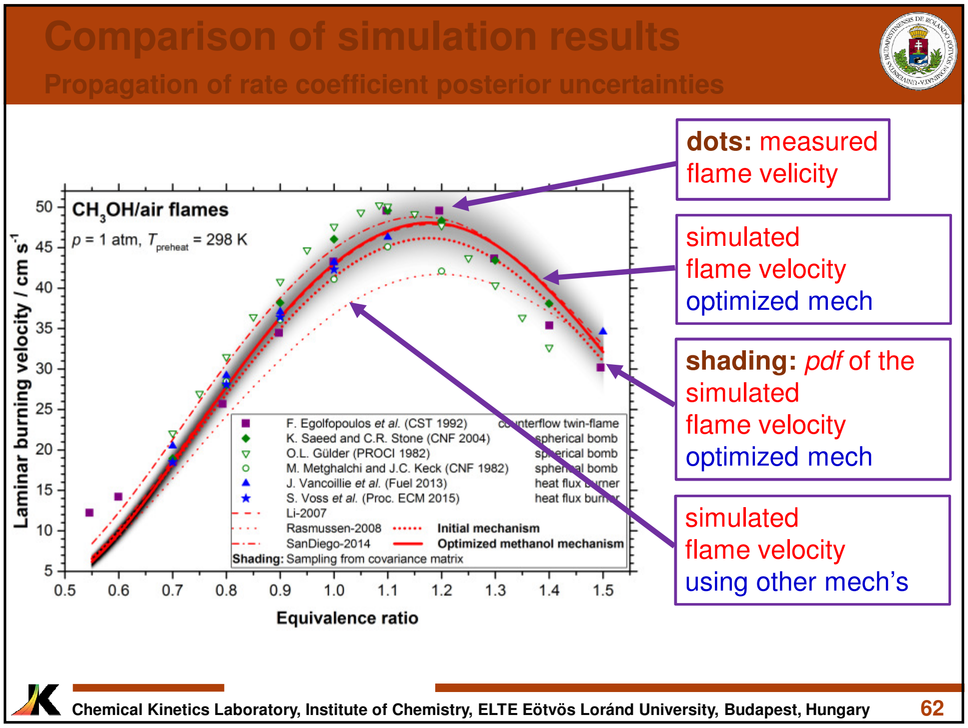
space of rate parameters

space of simulation results

model

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 velicity

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

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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/

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

What is RESPECTH?

ReSpecTh is an information system of the **MTA-ELTE Complex Chemical Systems Research Group**, prepared in collaboration with the **Laboratory of Molecular Structure and Dynamics** and the **Chemical Kinetics Laboratory** research laboratories of the Institute of Chemistry, Eötvös University, Budapest, Hungary.

If you are interested in data from reaction kinetics (Re), spectroscopy (Spec), or thermochemistry (Th), please click on RE, SPEC, or TH, respectively.

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