



COST is supported by the  
EU Framework programme  
Horizon 2020



# Validation and optimization of detailed combustion mechanisms

István Gy. Zsély

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



COST Training School on the Analysis of Combustion Mechanisms  
4-7 July, 2016 Budapest, Hungary Lecture 1-4



# On detailed combustion mechanisms

- Detailed mechanism contain elementary reactions and are used for the

## DESCRIPTION OF COMBUSTION CHEMISTRY

- understanding the underlying chemistry
  - making predictions
- 
- Technically, detailed mechanisms  
can be used **directly in simulations**  
OR  
can be simplified to various **reduced schemes**





# On mechanisms reduction

Lecture Wednesday 3-1 (Nagy)  
Reduction of reaction mechanisms 1  
(creation of a skeleton mechanisms: DRG, DRGEP, DRGEP-ASA, SEM)

Lecture Wednesday 3-2 (Tomlin)  
Reduction of reaction mechanisms 2  
(fitted models and species lumping)

Lecture Wednesday 3-3 (Goussis)  
Reduction of reaction mechanisms 3  
(methods based on time-scale separation: CSP)

Lecture Wednesday 3-4 (Goussis)  
Reduction of reaction mechanisms 4  
(methods based on time-scale separation: ILDM, ISAT, REDIM)

Lecture Thursday 4-1 (Goussis)  
Reduction of reaction mechanisms 5  
(methods based on time-scale separation: QSSA and PEA)





# On detailed combustion mechanisms

Researchers can find numerous detailed combustion mechanisms in the literature.

for hydrogen combustion

18 mechanisms between 2003-2013

for syngas combustion

18 mechanisms between 2003-2014

All applications **assume** that detailed combustion mechanisms are **ACCURATE.**

**Are they accurate???**

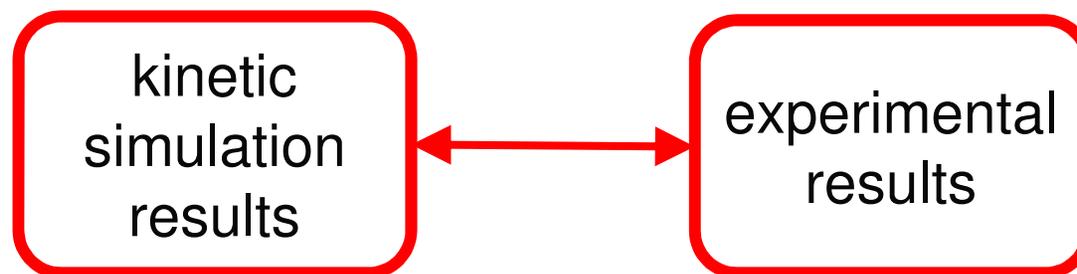


# Are all the detailed combustion mechanisms accurate?



## What is your guess?!

We have to COMPARE



## VALIDATION





# Possible aims of validation

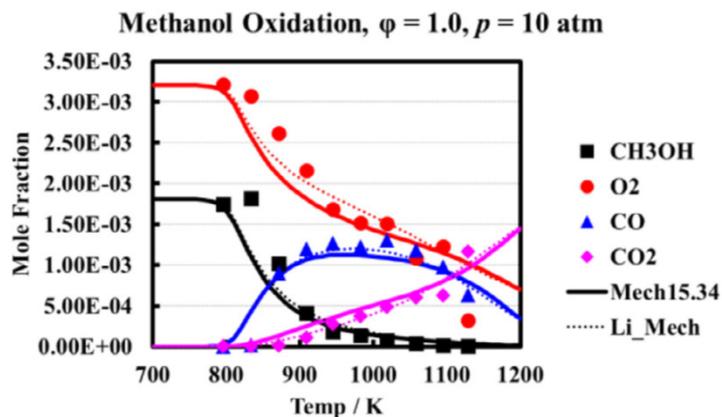
- Investigate the **suitability** of a published mechanism
  - Which mechanism is the best at my conditions?
- Provide a **guideline for users** of reaction mechanisms
  - Which are the good and bad mechanisms?
- Identify a **candidate** for further **improvement** through optimization
  - Which mechanism is the best one in general?
- Find **explanations** for potential **shortcomings** of the mechanisms in their actual **chemistry**
  - Why are the good mechanisms better than the others?



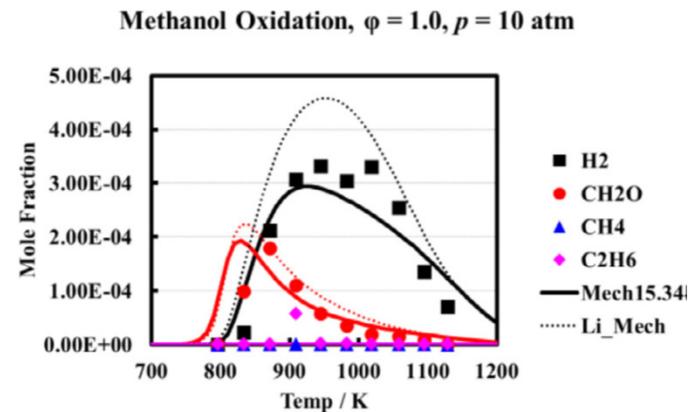
# Typical steps of the validation of a reaction mechanism



- Literature review of the field, looking for kinetic experiments
- Simulation of the experiments
- Visual comparison of the the kinetic simulation and the experimental results on graphs



(a) Major species



(b) Minor species

JSR species measurements for a mixture of 2000 ppm CH<sub>3</sub>OH and 3000 ppm O<sub>2</sub> and balance N<sub>2</sub> at a pressure of 10 atm and  $\tau = 0.5$  s.  
In: Burke et al. *Combustion and Flame* **165** (2016) 125-136



# Literature review for kinetic experiments



- Literature review of the field
  - Finding kinetic experiments
    - Review papers or papers dealing with mechanism development are utilized
      - A selected (well-known) measurement set is used, but rarely cited experiments are several times neglected
    - The original publications are cited, but not read, data are processed from another publication
      - Lack of critical evaluation, possible misinterpretation
    - Not all kind of kinetic experiments are used for validation (direct vs. indirect experiments)



# Different types of combustion experiments



## ▪ Direct measurements:

- Determination of the rate coefficient of a single elementary reaction
- Rate coefficients are published at a given temperature, pressure, and bath gas

## ▪ Theoretical (direct) determinations:

- TST/master equation calculations
  - The rate coefficients are published at given  $T$ ,  $p$
- Parameterized  $T$ ,  $p$  dependence of rate coefficient  $k$

## ▪ Indirect measurements:

- A property of the whole combustion system is measured
- Interpretation is based on a detailed mechanism
- *Examples:* Laminar burning velocities, ignition delays, concentration profiles



# Different types of combustion experiments



- **Direct measurements:**
  - Determination of the rate coefficient of a single elementary reaction
  - Rate coefficients are published at a given temperature, pressure, and bath gas
- **Theoretical (direct) determinations:**
  - TST/master equation calculations
  - The rate coefficients are published at given  $T$ ,  $p$
  - Parameterized  $T$ ,  $p$  dependence of rate coefficient  $k$

- Indirect measurements:

## For mechanism building and optimization

- Interpretation is based on a detailed mechanism
- *Examples:* Laminar burning velocities, ignition delays, concentration profiles



# Different types of combustion experiments



- Theoretical (direct) determinations:

## For mechanism validation and optimization

• The rate coefficients are published at given  $T, p$

→ Parameterized  $T, p$  dependence of rate coefficient  $k$

### ▪ Indirect measurements:

- A property of the whole combustion system is measured
- Interpretation is based on a detailed mechanism
- *Examples:* Laminar burning velocities, ignition delays, concentration profiles





# Simulation of indirect experiments

- Selection of the most appropriate **physical model** (experiment are typically designed in such a way that simple physical models describe them well)
- Selection of the corresponding **simulation code** (several simulation packages exist, there are simple and very complex ones, free and commercial)
- **Setting up simulations** based on the experimental apparatus and the experimental conditions (input file creation)
- **Running the simulations**



# Time needed for the simulations of indirect experiments



- Human time:
  - Interpretation of the experiment from a scientific paper, setting up the simulation  
appr. 1-5 minutes / exp. point
  - Achieving converged simulation and its collection from result files  
appr. 1-30 minutes / exp. point
- Computer time:
  - Simulation time  
appr. 0.1 s – 30 minutes / exp. point





# Automatization of the simulations

A few minutes / exp. point **seems not to be bad**, BUT

for the hydrogen combustion there are

**more than 2000 experimental points...**

Let's calculate!

It is **two weeks continuous work**, no sleeping, no eating...

And what if we have to **repeat the simulations?!**

Less human time, but still exhausting. (No food for a week?!)

**Automatization is needed!**



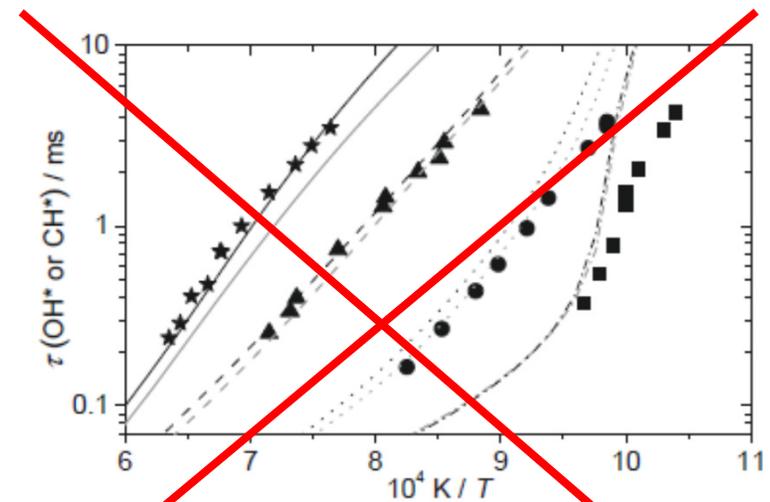
# Another issue: the comparison

We have thousands of experimental values and thousands of simulation results.

## How to compare so many data?

### The traditional way:

- Figures: only qualitative information
- Manual figure creation is time consuming
- It is quite hard to overview the results



J. Herzler, C. Naumann  
*Proceedings of the Combustion  
Institute* **32** (2009) 213–220  
Figure 4



# What can we do?

## How can an automatized simulation and validation framework work?

- The interpretation of the experiments should be done only once. The experimental data are converted to automatically and unambiguously interpretable files.
- Simulations run without human interaction.
- Results are collected, figures created automatically.
- Quantitative comparison of the simulation results and experimental data is performed.



# Automatically interpretable experimental files: the RKD format



The traditionally published experimental information should be converted to **an unambiguous, flexible data format**.

Based on preceding works we introduced the XML-based **ReSpecTh Kinetics Data format (RKD format)**

Practical session Thursday 4-1 (Varga)  
Encoding combustion experimental data  
Optima++

Hundreds of **RKD format** experimental files are shared in the **ReSpecTh Information system**.



# The ReSpecTh information system

Website: <http://respecth.hu/>



- **R**eaction kinetics
- high-resolution molecular **S**pectroscopy
- **T**hermochemistry data

- **S**earchable data
- **U**tility codes

## RESPECTH



### 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.

[About us](#)

[Register](#)





# Simulation framework

The simulation framework is a key in both, mechanism validation and optimization.

**We use our recently developed **Optima++** environment.**

Features and usage will be discussed in details in practical sessions:

Practical session Wednesday 3-2 (Olm)  
Validation of detailed combustion mechanisms  
outgen, Optima++

Practical session Thursday 4-1 (Varga)  
Encoding combustion experimental data  
Optima++

Practical session Thursday 4-2 (Varga)  
Optimization of detailed combustion mechanisms  
Optima++



# Main features of the OPTIMA environment

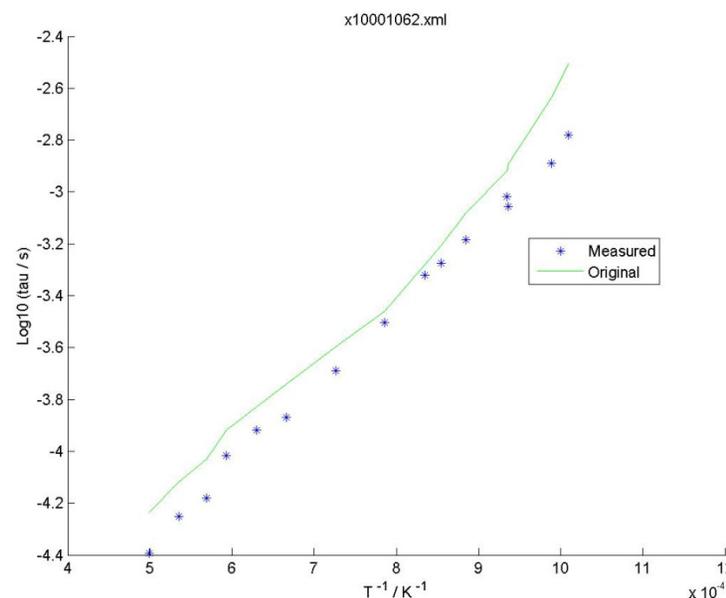


Handles multiple RKD files in one run.

Subset of experimental points can be selected in data series.

Can start simulations parallel in a multicore computer.

Instead of solving the kinetic differential equation system response surfaces can be used.



Experiment: M. C. Krejci; O. Mathieu; A. J. Vissotski; S. Ravi; T. G. Sikes; E. L. Petersen; A. Keromnes; W. K. Metcalfe; H. J. Curran, Proceedings of ASME Turbo Expo 2012-GT2012, June 11-15, Copenhagen, Denmark 2012, Paper GT2012-69290, Table A6  
Model: SanDiego 2014



# How to compare thousands of results?



Instead of figures and verbal comparison

**quantitative functions**

have to be used to characterize the goodness of simulations.

**Error functions / deviation functions**





# General features of the error function

- The goodness of the simulation results must be measured quantitatively
  - **Difference of modeled and experimental value**
- No difference between over/underprediction
  - **Square is used**
- Different type of measurements should be comparable
  - **Transformation (normal or logarithmical scale)**
  - **Division by the standard deviation/scatter**
  - **The indirect and direct experiments are not distinguished**





# General features of the error function

- Has to be independent of the number of experimental point in the data series
  - **Division by the number of data points of the experimental series**
- Error function of different sets of experiments should be comparable
  - **Division by the number of datasets**
- The error function values should be meaningful
  - **Comparison of the difference with the estimated scatter**



# The error function

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

**Number of data series**

(reduction to a single value)

**Number of points**

(division makes data series differing in size comparable)

**Estimated standard deviation / scatter**

(makes different types of experiments comparable, accounts for different reliability of data)

**Difference of simulated and experimental value**

(characterized the prediction of one measured value)

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

**Transformation**

(comparison of experiments with absolute and relative errors)

The **agreement between simulations and measurements** can be well characterized quantitatively by this error function

# The absolute deviation function

## Absolute deviation of a single data point

(similarity can also be described by correlating these  $D_{ij}$  values)


$$D = \frac{1}{N} \sum_{i=1}^N \frac{1}{N_i} \sum_{j=1}^{N_i} \left( \frac{Y_{ij}^{\text{sim}} - Y_{ij}^{\text{exp}}}{\sigma(Y_{ij}^{\text{exp}})} \right)$$

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

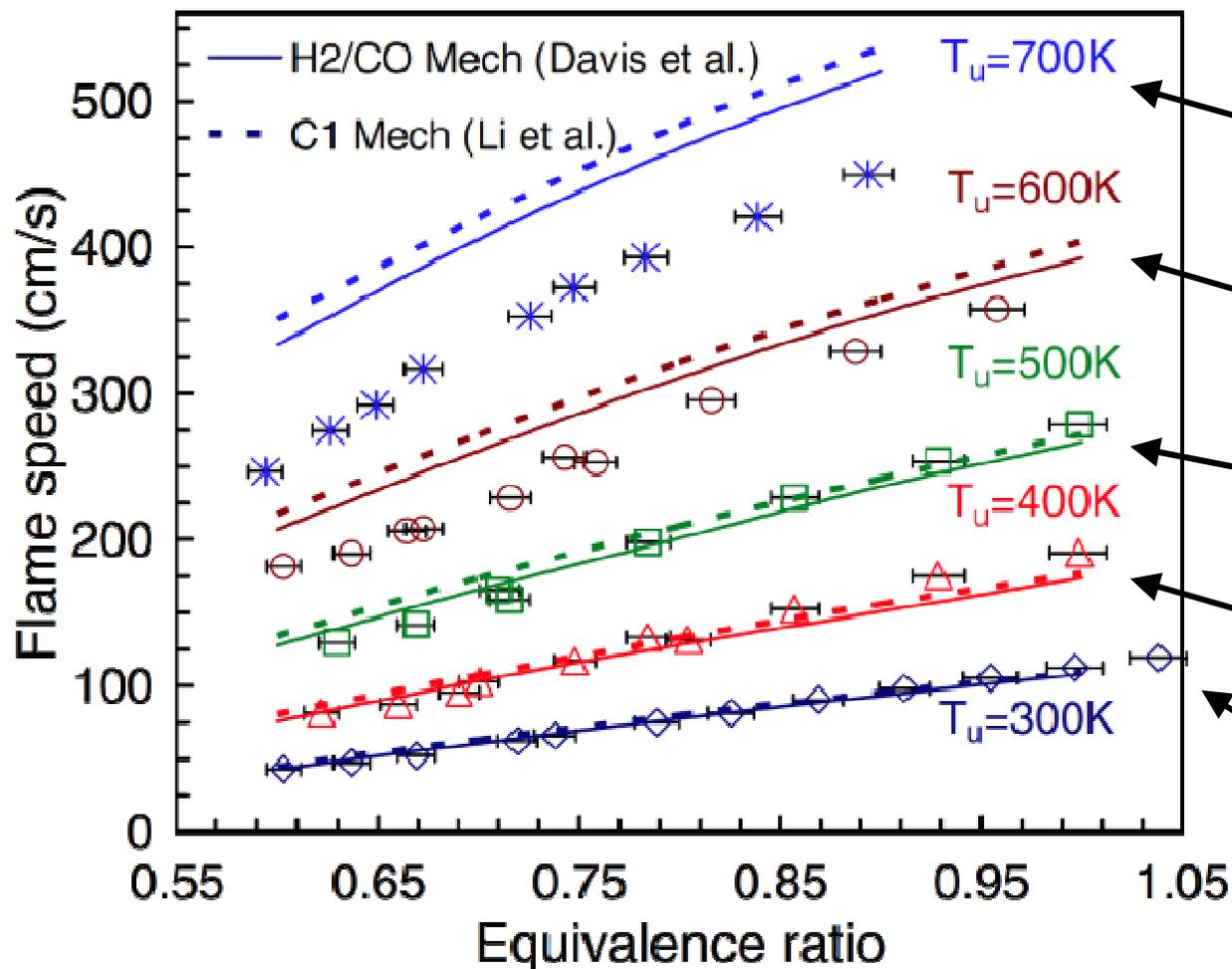
→ Captures trends such as under- / over-prediction

The **similarity of simulation results using different mechanisms** can be well characterized quantitatively by this absolute deviation



# Example: Laminar burning velocities

Natarajan *et al.*, Proc. Comb. Inst. **32**, 1261-1268, (2009). Fig. 3



	<i>E</i>	<i>D</i>
	998	+62.6
	1603	+79.6
	21.94	+29.2
	39.96	+40.2
	1.46	+4.3
	2.72	+11.2
	3.29	+0.5
	4.67	+4.7
	2.15	+1.1
	5.19	+3.5

**“The measured flame speeds are in good agreement (within 10%) with both model predictions, up to a preheat temperature of about 500 K.”**

Davis *et al.*

Li *et al.*



# How to compare thousands of results?



	Advantage	Drawback
<b>Error function</b>	Characterizes the agreement between the simulations and experiments quantitatively well  Can be used as objective function in optimization	Sign of deviations is lost
<b>Absolute deviation function</b>	Captures systematical under- or over-predictions	Positive and negative values can cancel each other

The accuracy of a detailed reaction mechanism can be quantitatively characterized using these measures.

**Moreover, the performance of different reaction mechanisms becomes easily comparable.**



# outgen: a simulation result post-processor



- Experimental conditions, results and simulation results are read from plain text files
- Multiple mechanisms can be handled simultaneously
- The error function and the absolute deviation function are automatically calculated for a subset of points selected
- Selection of data to be included in the comparison by applying certain filtering criteria  
(*e.g.* by measurement type, experiment type, conditions)

**More details on outgen:**  
Practical session  
Wednesday 3-2 (Olm)



# Case study: Hydrogen combustion

- Hydrogen is an important fuel itself  
fuel of large rockets  
„carbon-free economy”
- Hydrogen/air mixtures present safety hazard in the industry  
the most memorable example:  
explosion of the Fukushima reactor building
- The cores of the syngas and high temperature hydrocarbon combustion mechanisms are the H/O reactions



# Literature review for the hydrogen combustion



**Our aim was to collect ALL hydrogen combustion experimental data ever published**

Reality: we collected the data published after about 1960

**BUT:** includes all data used for testing mechanisms

• Ignition delays – shock tube	770 data points in 53 datasets
• Ignition delays – RCM	229 data points in 20 datasets
• Laminar burning velocities	631 data points in 73 datasets
• Species profiles – JSR	152 data points in 9 datasets
• Species profiles – flow reactor	389 data points in 17 datasets

## Wide range of conditions

- Temperature: 800 K – 2300 K      Pressure 0.1 bar – 65 bar
- Equivalence ratio 0.2 – 5.0

C. Olm, I. Gy. Zsély, R. Pálvölgyi, T. Varga, T. Nagy, H. J. Curran, T. Turányi  
[Comparison of the performance of several recent hydrogen combustion mechanisms](#)  
*Combustion and Flame*, **161**, 2219-2234 (2014)





# Selection of mechanisms

**All hydrogen mechanisms published after 2003** were investigated

GRI-Mech 3.0 (1999) was added in this study, since it is a widely used mechanism

Only CHEMKIN-format mechanisms were investigated

The mechanisms were collected from ... (in this order)

- (1) Electronic Supplement of the original publication
- (2) web site of the authors
- (3) e-mail request from the authors

Always the original THERMO and TRANSPORT files were used!



# Hydrogen combustion mechanisms



Mechanism (chronological order)	Species number (orig.)	Reactions number (orig.)
GRI3.0-1999	10 (53)	29 (325)
Dagaut-2003	9 (132)	21 (922)
Ó Conaire-2004	10	21
Davis-2005	11 (14)	25 (38)
Zsély-2005	10 (13)	32 (44)
SaxenaWilliams-2006	11 (14)	21 (30)
Ahmed-2007	10 (246)	20 (1284)
Li-2007	11 (21)	25 (93)
Sun-2007	11 (15)	32 (48)
USC-II-2007	10 (111)	28 (784)
Konnov-2008	10	33
Rasmussen-2008	10 (24)	30 (105)
Starik-2009	12 (16)	26 (44)
NUIG-NGM-2010	11 (293)	21 (1593)
SanDiego-2011	11 (50)	21 (244)
Hong-2011	10	31
CRECK-2012	11 (14)	21 (34)
Burke-2012	11	27
Kéromnès-2013	12 (17)	33 (49)

- 19 mechanisms published since 1999

- 4 developed for hydrogen only

- 15 developed for larger systems

- He (and Ar) is not defined



# Detailed comparison of the reaction mechanisms

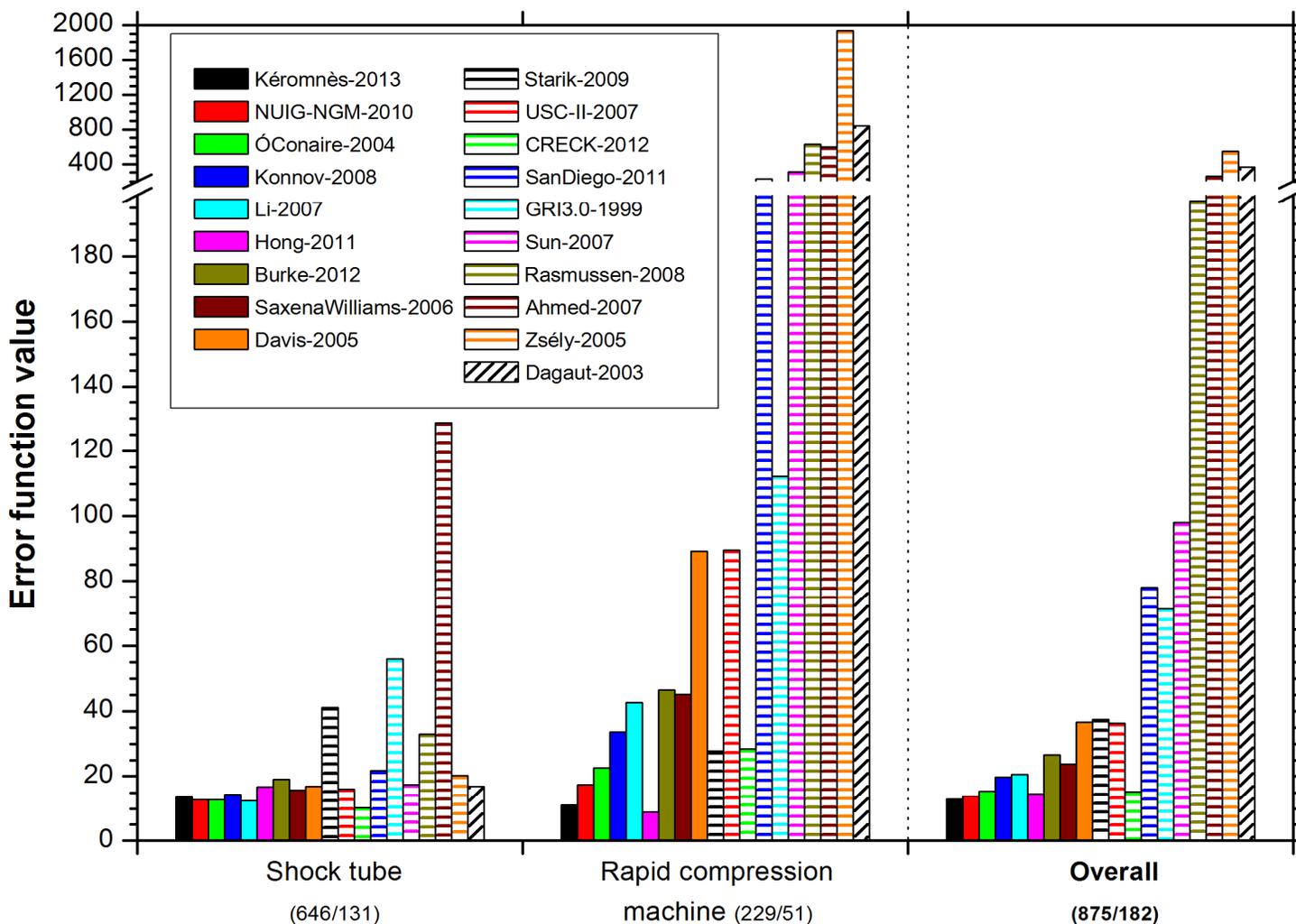


No.	Mechanism ID	Ref.	Species number (orig.)	Ar/He	Reactions number (orig.)	Error function values					
						Ignition delay times	JSR conc.	Flow reactor conc.	Flame $v_L$ no He	Overall no He	Overall
1	Kéromnès-2013	[4]	12 (17)	x/x	33 (49)	11.9	3.0	13.3	13.9	12.2	12.4
2	NUIG-NGM-2010	[20]	11 (293)	x/x	21(1593)	14.0	3.0	7.3	20.2	14.8	13.3
3	ÓConaire-2004	[9]	10	x/-	21	15.4	3.0	8.2	18.5	15.0	–
4	Konnov-2008	[10]	10	x/-	33	19.7	3.1	10.9	15.2	16.3	–
5	Li-2007	[21]	11 (21)	x/x	25 (93)	20.7	3.0	7.8	16.0	16.8	15.8
6	Hong-2011	[12]	10	x/-	31	14.5	3.0	8.1	28.5	17.9	–
7	Burke-2012	[11]	11	x/x	27	26.6	3.1	3.9	14.6	18.9	16.7
8	SaxenaWilliams-2006	[13]	11 (14)	x/x	21 (30)	23.8	3.0	28.3	16.5	20.5	19.0
9	Davis-2005	[14]	11 (14)	x/x	25 (38)	36.7	3.0	4.9	16.4	24.7	21.8
10	Starik-2009	[15]	12 (16)	x/x	26 (44)	37.4	3.4	3.8	24.4	27.7	24.7
11	USC-II-2007	[22]	10 (111)	x/-	28 (784)	36.2	3.0	4.7	26.1	27.7	–
12	CRECK-2012	[16]	11 (14)	x/x	21 (34)	15.2	2.9	21.4	56.9	29.1	25.6
13	SanDiego-2011	[23]	11 (50)	x/x	21 (244)	78.0	3.0	27.7	16.5	47.7	42.0
14	GRI3.0-1999	[24]	10 (53)	x/-	29 (325)	71.4	2.4	11.6	32.0	48.0	–
15	Sun-2007	[17]	11 (15)	x/x	32 (48)	97.9	3.1	25.4	26.7	61.0	53.8
16	Rasmussen-2008	[18]	10 (24)	x/-	30 (105)	197.1	3.0	17.8	35.4	113.1	–
17	Ahmed-2007	[25]	10 (246)	x/-	20 (1284)	257.9	3.1	3.9	20.7	137.4	–
18	Zsély-2005	[19]	10 (13)	x/-	32 (44)	544.3	3.2	15.6	26.0	284.5	–
19	Dagaut-2003	[26]	9 (132)	-/-	21(922)	–	3.1	4.9	–	–	–



# Error function values

Depending on the type of ignition delay measurement facility

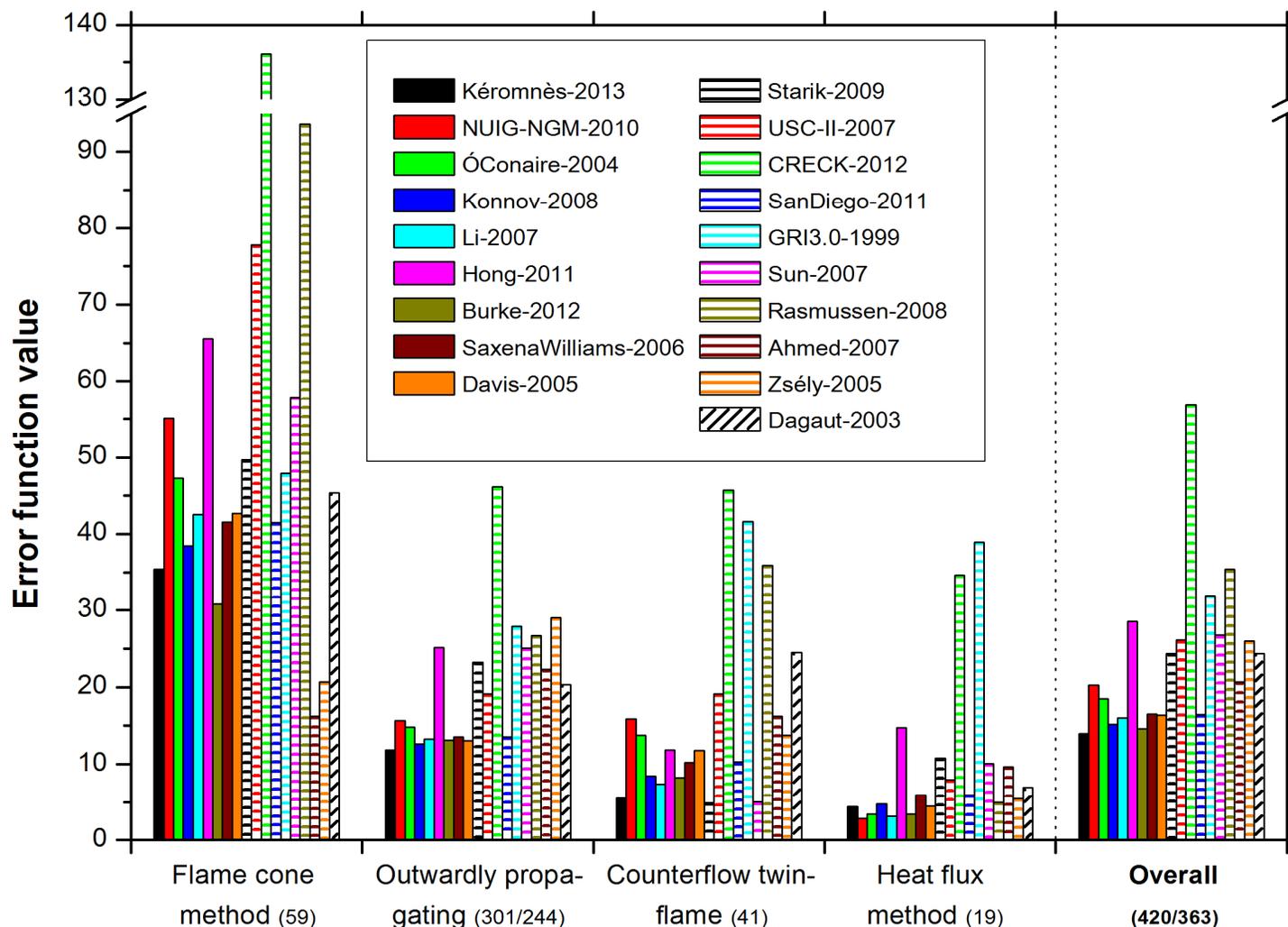


Ignition delay time: Influence of experimental method



# Error function values

Depending on the type of burning velocity measurement facility

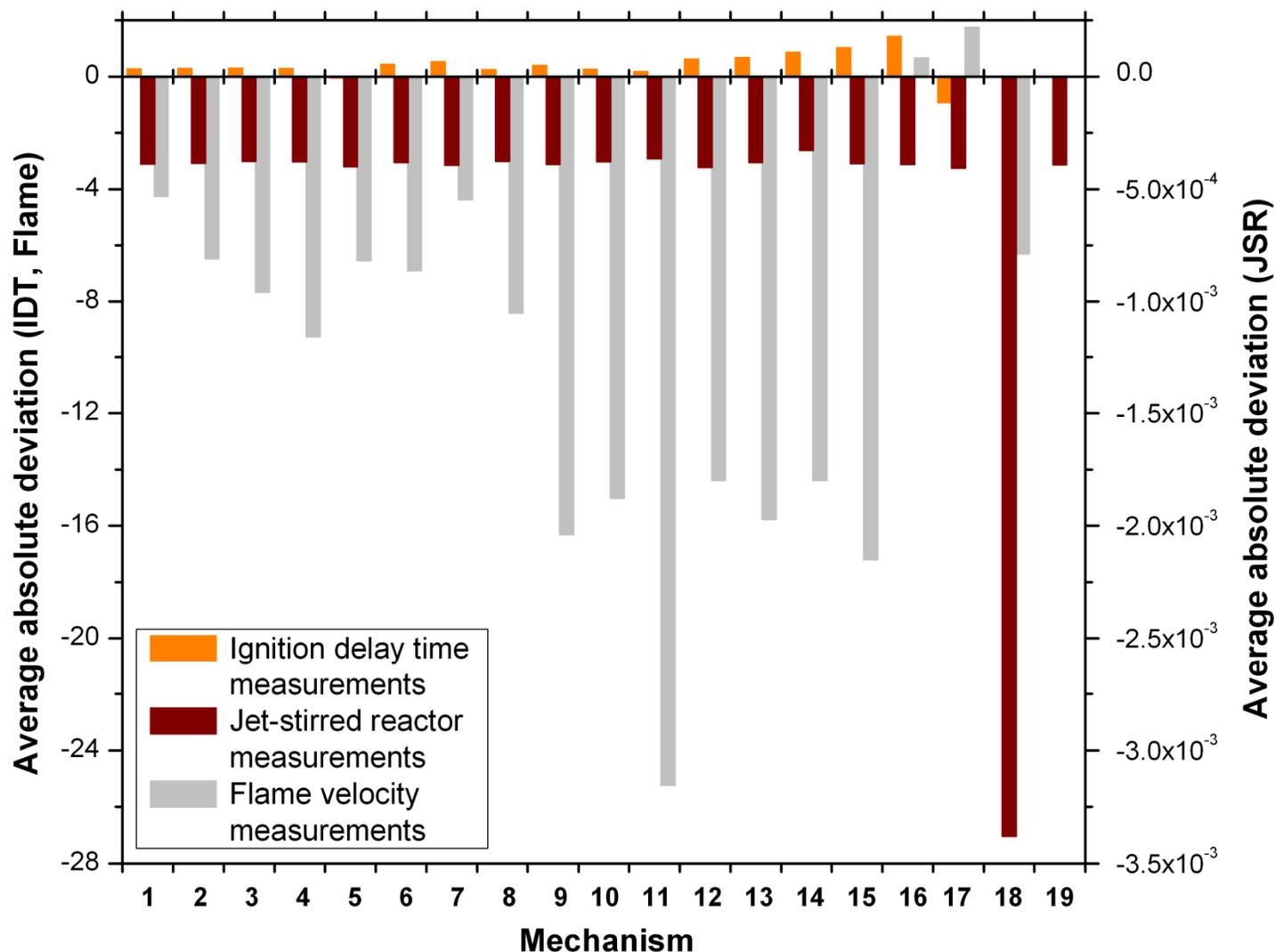


Flame velocity: Influence of experimental method

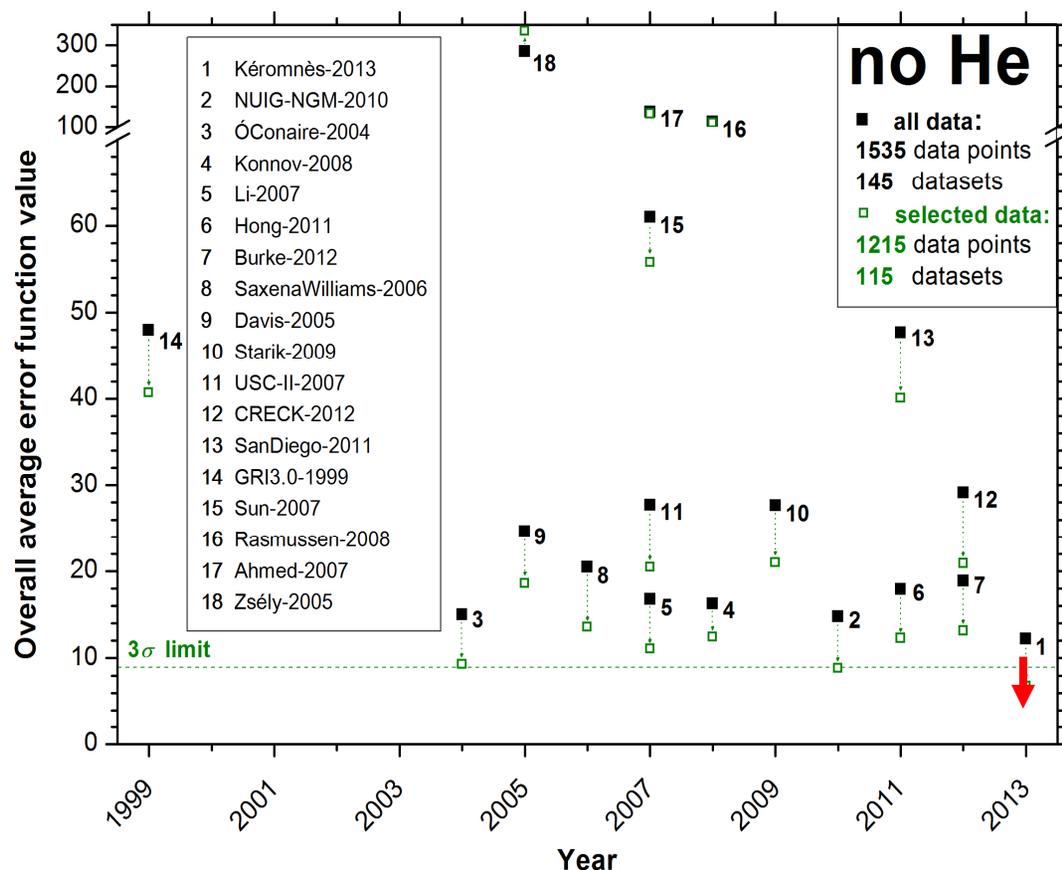


# Absolute deviation function values

Depending on the type of indirect experiments



# How the accuracy evolved in time?



How can be the results improved?

**Optimization!**

Overall performance of the mechanisms. All diluents except He.

**black square ■** : all experimental data

**green square □** : only the reproducible experiments ( $E_i \leq 9$  with at least one mechanisms)





# Possible aims of optimization

- Develop a **mechanism** that **describes better** a large number of combustion **experiments** than the available mechanisms
  - What is the best parameter set for a given mechanism structure?
- Approach „real” **physical values** of the reaction rate coefficients rather than just fitting them
  - How to keep the physical meaning of the parameter?
- Describe the **remaining uncertainties** of the obtained model
  - How accurate the determined parameters are?



# The pioneers of mechanism optimization



Parameter optimization techniques to improve detailed combustion models was first proposed by

**Frenklach and Miller** [1–3].

The algorithm was described in the article of **Frenklach et al.** [4].

Most successful optimized natural gas combustion mechanism:

**GRI-Mech 3.0** [5].

[1] D. Miller; M. Frenklach, *Int. J. Chem. Kinet.* 1983, 15, 677–696.

[2] M. Frenklach, *Combust. Flame* 1984, 58, 69–72.

[3] M. Frenklach; D. L. Miller, *AIChE J.* 1985, 31, 498–500.

[4] M. Frenklach; H. Wang; M. J. Rabinowitz, *Prog. Energy Combust. Sci.* 1992, 18, 47–73.

[5] G. P. Smith; D. M. Golden; M. Frenklach; N. W. Moriarty; B. Eiteneer; M. Goldenberg; C. T. Bowman; R. K. Hanson; S. Song; W. C. Gardiner; V. V. Lissianski; Z. Qin GRI-Mech 3.0. [http://www.me.berkeley.edu/gri\\_mech/](http://www.me.berkeley.edu/gri_mech/)



# Data collaboration

Frenklach and co-workers



Frenklach and co-workers further developed the mechanism optimization approach toward **data collaboration** [1–5].

Provided an implementation of the method on the **PrIMe website** [6],

and recommended the usage of the **PrIMe data format** [6].

- [1] R. Feeley; P. Seiler; A. Packard; M. Frenklach, *J. Phys. Chem. A* 2004, 108, 9573–9583.
- [2] M. Frenklach; A. Packard; P. Seiler; R. Feeley, *Int. J. Chem. Kinet.* 2004, 36, 57–66.
- [3] R. Feeley; M. Frenklach; M. Onsum; T. Russi; A. Arkin; A. Packard, *J. Phys. Chem. A* 2006, 110, 6803–6813.
- [4] M. Frenklach, *Proc. Combust. Inst.* 2007, 31, 125–140.
- [5] X. Q. You; T. Russi; A. Packard; M. Frenklach, *Proc. Combust. Inst.* 2011, 33, 509–516.
- [6] M. Frenklach PrIMe Webpage. <http://www.primekinetics.org/>
- [7] X. You; A. Packard; M. Frenklach, *Int. J. Chem. Kinet.* 2012, 44, 101–116.



# Utilizing polynomial chaos expansions

Wang and co-workers



Another series of mechanism optimization papers was published by Wang and his co-workers [1-5].

Their method of **uncertainty quantification and minimization using polynomial chaos expansions**

proposed by Sheen and Wang [5] also provides a way to calculate the covariance matrix of the fitted parameters.

These methods were summarized in a recent review article [6].

[1] S. G. Davis; A. V. Joshi; H. Wang; F. Egolfopoulos, Proc. Combust. Inst. 2005, 30, 1283–1292.

[2] W. J. Qin; V. V. Lissianski; H. Yang; W. C. Gardiner; S. G. Davis; H. Wang, Proc. Combust. Inst. 2000, 28, 1663–1669.

[3] D. A. Sheen; X. You; H. Wang; T. Lovas, Proc. Combust. Inst. 2009, 32, 535–542.

[4] D. A. Sheen; H. Wang, Combust. Flame 2011, 158, 645–656.

[5] D. A. Sheen; H. Wang, Combust. Flame 2011, 158, 2358–2374.

[6] H. Wang; D. A. Sheen, Prog. Energy Combust. Sci. 2015, 47, 1–31.



# Main features of the methods of

Frenklach *et al.* and Wang *et al.*



- a small number of optimization targets are selected
- the most influential rate parameters (called “active parameters”) are identified using local sensitivity analysis (A-factors of the rate expressions, third-body collision efficiency parameters, enthalpies of formation of certain species)
- polynomial surrogate models (“response surfaces”) are used for each optimization target to express the simulation result as a function of the values of the active parameters





# Their objective functions

In the development of GRI Mech. 3.0 the objective function was composed directly from values of different experiments in arbitrary units. It worked for them, but can not be utilized in another optimization work.

Wang et al. started to use a much more supported error function:

$$L^2 = \sum_i [(\mu_{i, expt} - \mu_{i, calc}) / \sigma_i]^2$$



# GRI Mech. 3.0

Reproduced from <http://combustion.berkeley.edu/gri-mech/>



## SOME CAUTIONARY NOTES

We want to warn you about several important aspects of GRI-Mech.



**PLEASE DO NOT MAKE ANY SUBSTITUTIOS**

Or if you **MUST** so, be very careful. **GRI-Mech has been optimized as a whole**, and should be used just as you get it if you want to exploit its ability to model natural gas combustion. You will not surpass the overall performance we get for natural gas combustion by adjusting any 'sensitive' reaction rate constant expressions.

**Any substitution** of 'better' rate constant expressions or thermochemical or transport coefficient values, or outright removal of species or reactions, **will put you at risk of getting significantly deteriorated performance of the mechanism** when tested against the available spectrum of natural gas combustion data.

**Reason: the not well-composed error function lead to physically unrealistic model.**





# Enhanced approaches

Both Frenklach et al. and Wang et al. found that after optimization many of the **A-factors** obtained were at the edges of their assigned uncertainty intervals.

To address this issue

- Frenklach *et al.* moved to data collaboration (constraints, feasible sets and their estimations).
- Wang *et al.* modified the objective function, the deviation of the *A*-factors from their initial values is penalized:

$$\Phi = \sum_r [(\mu_{r, \text{expt}} - \mu_{r, \text{calc}}) / \sigma_r]^2 + \sum_k 2x_k^2$$



# Mechanism optimization using Optima++



## Main steps of optimization:

- Selection of the experimental data used for the optimization (“targets”)
- Assembling an initial mechanism
- Deciding on parameters to be optimized
- Estimating prior rate coefficient uncertainties
- Creating restart files and/or response surfaces
- Selection of additional optimization targets (direct and theoretical rate determinations), exclusion of targets if needed
- Error function minimization



# Selection of the experimental data used for the optimization



## Fundamental decision!

For a **special case** you may use a **limited set of experiments**, but the **validity** of the optimized mechanisms is guaranteed only for limited conditions.

For **general purposes** you have to select a **wide range of experiments**, a **comprehensive** set covering all possible conditions.

**1<sup>st</sup> question:** What is the planned validity range of your mechanism?

**2<sup>nd</sup> question:** Is this range sufficiently covered by the available experiments?



# Assembling an initial mechanism



First candidate mechanism: the best mechanism from the validation on the selected condition range.

**BUT!**

**The structure of your mechanism will be fixed from this stage onwards.**

Structure of the mechanism: the set of species and reactions

You cannot add species or missing pathways during the optimization. Missing species/reactions can distort the fitted parameters due to compensation effects.

If you decide later to correct the structure of your mechanism the whole procedure must be repeated!





# Deciding on parameters to be optimized

The parameters to be optimized must be sensitive.

Sensitive parameter: its change significantly modifies the simulation result

Also called “active parameter”.

Simplest method: local sensitivity analysis

Lecture Monday 1-2 (Tamás Turányi)

Local sensitivity analysis



# Estimating prior rate coefficient uncertainties



Lecture Monday 1-3 (Tamás Turányi)  
Uncertainty of data and parameters  
uncertainty of combustion measurements,  
rate coefficients, Arrhenius parameters and  
thermodynamic data

Practical session Monday 1-1 (Valkó)  
Calculation of the prior uncertainty of rate coefficients  
*u-Limits*, UBAC, JPDAP and SAMAP



# Creating restart files and/or response surfaces



Optimization requires  $\sim 10^4$ - $10^5$  evaluations of the error function.

**Long simulation times make the error function minimization practically impossible,**  
therefore, speeding up the simulations is more than welcome.

**BUT it should not ruin the accuracy!**

- Flame calculations can be speeded up using restart files
- Response surfaces can be utilized





# Restart files for flame simulations

Some flame solvers use restart files for obtaining a solution (FlameMaster) or obtaining this solution faster (CHEMKIN/PREMIX).

Good starting estimations in restart files enhances the simulations a lot.

No additional error is introduced, since the kinetic differential equation system is solved, just faster.

This leads to a speed-up of approx. one order of magnitude.

**Good, but not enough.**

1000 flames,  $10^6$  flame simulations still thousands of CPU hours...





# Response surfaces

If the kinetic differential equation system is not solved:  
**significant speed-up!**

The solution is recovered from a database or calculated from algebraic equations: Solution mapping / response surfaces

Some additional error is introduced, but VERY FAST!  
2-4 order of magnitude speed-up.

Different methods are available!





# Response surfaces – different methods

- Frenklach et al.: solution mapping
  - M. Frenklach; H. Wang; M. J. Rabinowitz, *Prog. Energy Combust. Sci.* 1992, **18**, 47–73.
- Sheen and Wang: polynomial chaos expansion
  - Sheen; H. Wang, *Combust. Flame* 2011, **158**, 2358–2374.
- Turányi et al.: orthonormal polynomial expansion
  - T. Turányi, *Computers Chem.* 1994, **18**, 45–54.

More details: Lecture Wednesday 3-2 (Tomlin)  
Reduction of reaction mechanisms 2  
(fitted models and species lumping)



# Selection of additional optimization targets, exclusion of targets if needed



Indirect measurements are commonly used optimization targets, but some of them cannot be utilized:

- Convergence problems
- Facility effect
- Too slow calculations → restart files / response surfaces
- Inaccurate response surfaces (if used)

Direct and theoretical rate determinations are further potential optimization targets

- The active parameters / reactions involves direct rate determination experiments. Most optimization methods do not use them or only indirectly, but they can be added to the optimization directly



# The error function used in Optima++



The objective/error function used is the error function already discussed in the first part (validation) of this lecture:

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



# Error function minimization

How to optimize in a high-dimensional space?



## Global optimization

Hard to find the GLOBAL minimum,  
although LOCAL minimums can be reached.

## Curse of dimensionality

We have typically 10-60 active parameters.  
10 points in each dimension means  $10^{10} - 10^{60}$  samples...

**No guarantee to find the best parameter set.**



# How to optimize in a high-dimensional space?



**Several methods, dedicated scientific journal!**

## Journal of Global Optimization

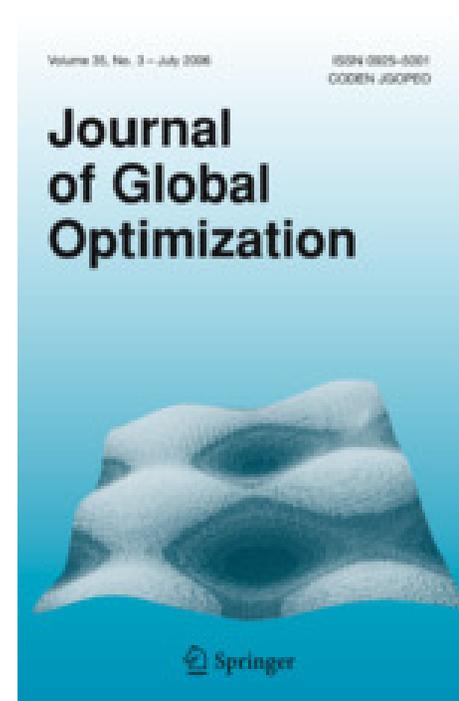
An International Journal Dealing with Theoretical and Computational Aspects of Seeking Global Optima and Their Applications in Science, Management and Engineering

Editor-in-Chief: Sergiy **Butenko**

ISSN: 0925-5001 (print version)

ISSN: 1573-2916 (electronic version)

Journal no. 10898



# The optimization algorithm used in Optima++



- Generate random sample of rate parameters
- Evaluate error function  $E$  at each parameter set
- Select parameter set that gave the lowest  $E$  values as the present optimal set
- Calculate new covariance matrix of the parameters (optional)
- If no better parameter set (no lower  $E$ ) was found, focus on a smaller parameter range
- If a better parameter set (lower  $E$ ) found, start the next round of sampling in a larger parameter range



# A possible hierarchical optimization strategy



Not all parameters should be optimized from the beginning!

Chemistry is the same everywhere!

- Hierarchy of the detailed combustion mechanism
- First, the most influential parameters are optimized, but only roughly
- Reactions (and the corresponding experiments) are added one by one and optimized first separately, later altogether



# Posterior uncertainty calculation

Provides information on the reliability of the fitted parameters.

Takes into account the systematic deviations of experiments.

The covariance matrix of the estimated parameters  $\Sigma_p$  is calculated at the optimal solution:

Covariance matrix of  
experiments



Discrepancy between  
experiments and model



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

$\Sigma_p \rightarrow$  posterior  $f(T)$  functions

# Case study: Optimization of a hydrogen combustion mechanism



Published in:

T. Varga, T. Nagy, C. Olm, I.Gy. Zsély, R. Pálvölgyi, É. Valkó, G. Vincze, M. Cserhádi, H.J. Curran, T. Turányi:

[Optimization of a hydrogen combustion mechanism using both direct and indirect measurements](#)

*Proc. Combust. Inst.*, **35**, 589-596 (2015)



# Selection of the experimental set for the optimization to be performed



**A comprehensive set of experiments was selected from the literature:**

- Ignition delays – shock tube                      786 data points in 54 datasets
- Ignition delays – RCM                                      229 data points in 20 datasets
- Laminar flame speeds                                      631 data points in 73 datasets
- Species profiles – JSR                                      149 data points in 9 datasets
- Species profiles – flow reactor                      372 data points in 16 datasets

**The experiments cover typical conditions of hydrogen combustion:**

- Temperature:                                      800 K – 2300 K
- Pressure:    0.1 bar – 65 bar
- Equivalence ratio:                                      0.2 – 5.0





# Assembling an initial mechanism

Based on a comprehensive mechanism comparison study, the best performing **Kéromnès-2013 mechanism** was selected as the initial mechanism.

A. Kéromnès, W.K. Metcalfe, K.A. Heufer, N. Donohoe, A.K. Das, C.-J. Sung, J. Herzler, C. Naumann, P. Griebel, O. Mathieu, M.C. Krejci, E.L. Petersen, W.J. Pitz, H.J. Curran  
*Combust. Flame* **160** (2013) 995–1011.

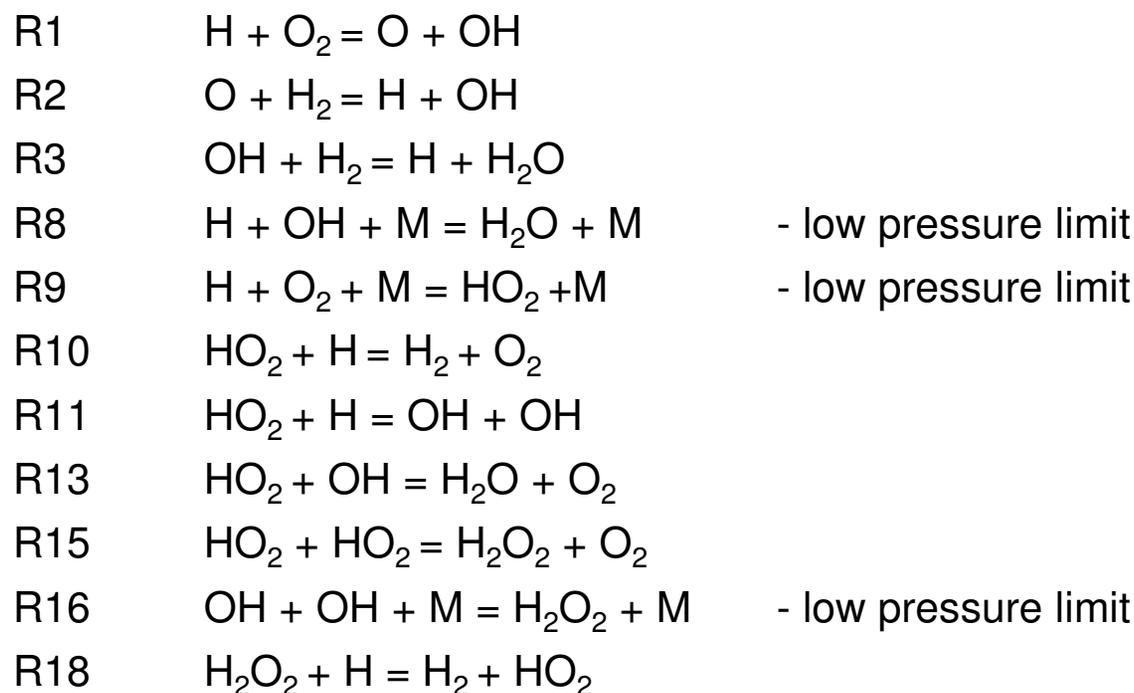




# Deciding on parameters to be optimized

**Local sensitivity analysis** was used to identify the effective („active”) parameters

→ **11 elementary reaction steps selected for optimization**

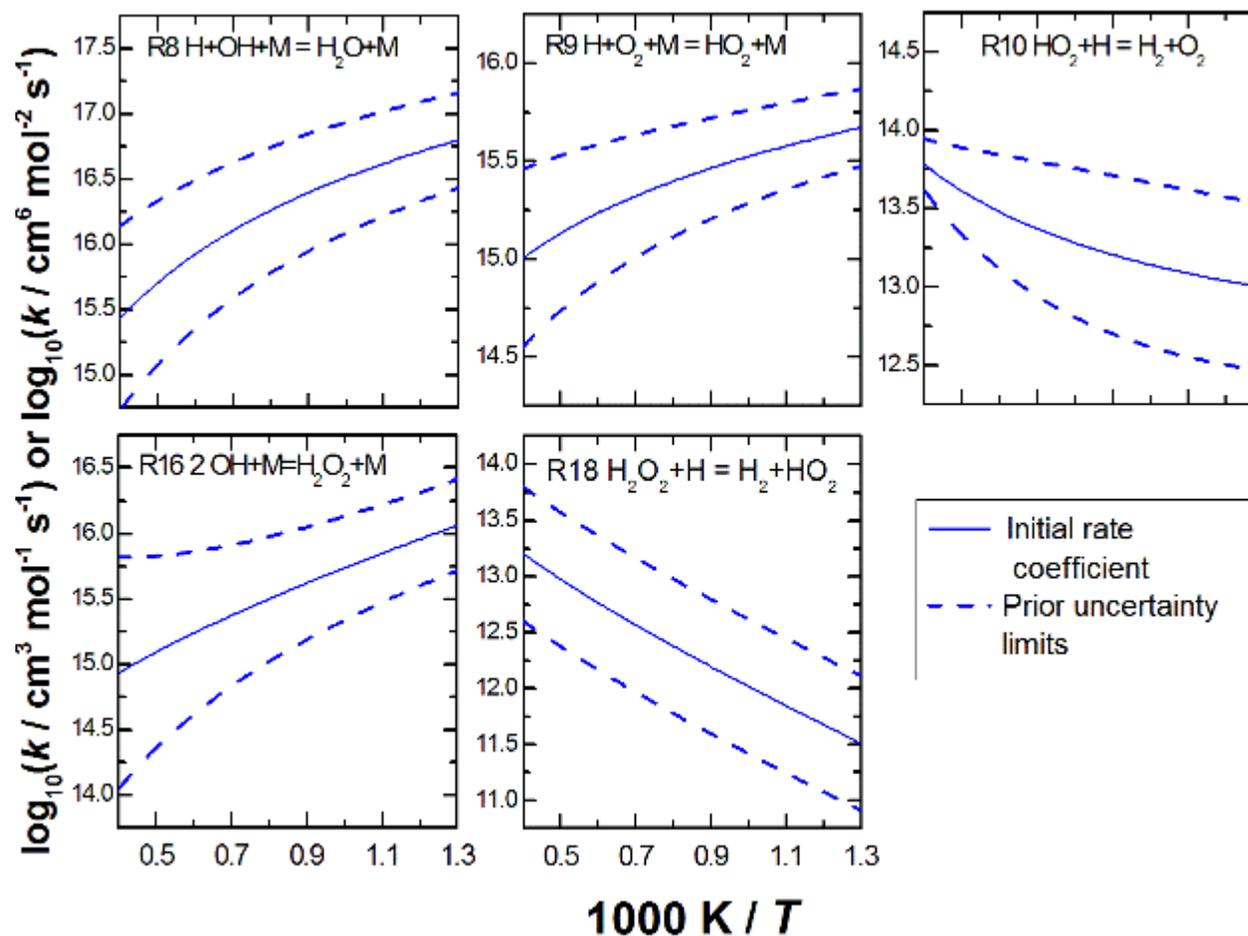


# Estimating prior rate coefficient uncertainties



Based on direct measurements and theoretical calculations,  $f(T)$  functions consistent with the Arrhenius expression are determined.

The shape and the prior *pdf* of the uncertainty domain of Arrhenius parameters are stored in their prior covariance matrix.





# Response surfaces

- **Both for ignition and laminar burning velocity experiments**
- **10,000 samples** of the active parameters
  - Different parameters at each condition, based on sensitivity analysis
- **Up to 4<sup>th</sup> order** polynomials were fitted
- **100x to 10,000x times faster simulations**
- Accuracy of the polynomials was tested against a new sample, which was not used for polynomial creation
  - **Maximum allowed deviations:  $\Delta \ln(\tau/s)_{\max} = 0.2$ ;  $\Delta v_l_{\max} = 2$  cm/s**
- About **80% of all data points** could be fitted accurately
  - In the final optimization only the flame response surfaces were used (the ignition delay times were calculated with direct integration)





# Final selection of optimization targets

## Some data points were excluded

- Flames without accurate response surfaces
- Flow reactor experiments – need time shift for interpretation; introduces a free parameter and causes under prediction of uncertainty
- Long ignition delays measured in shock tubes – Facility effects cannot be described without special measurements.
- Datasets that could not be reproduced within  $4\sigma$  uncertainty after a preliminary optimization

## Final set of optimization targets

- |  |                                 |
|--|---------------------------------|
| • Ignition measurements in shock tubes | 566 data points in 43 datasets  |
| • Rapid compression machines           | 219 data points in 19 datasets  |
| • Burning velocity measurements        | 364 data points in 59 datasets  |
| • Direct rate coefficient measurements | 1749 data points in 59 datasets |

**In total, 2898 experimental data points were used for the optimization**



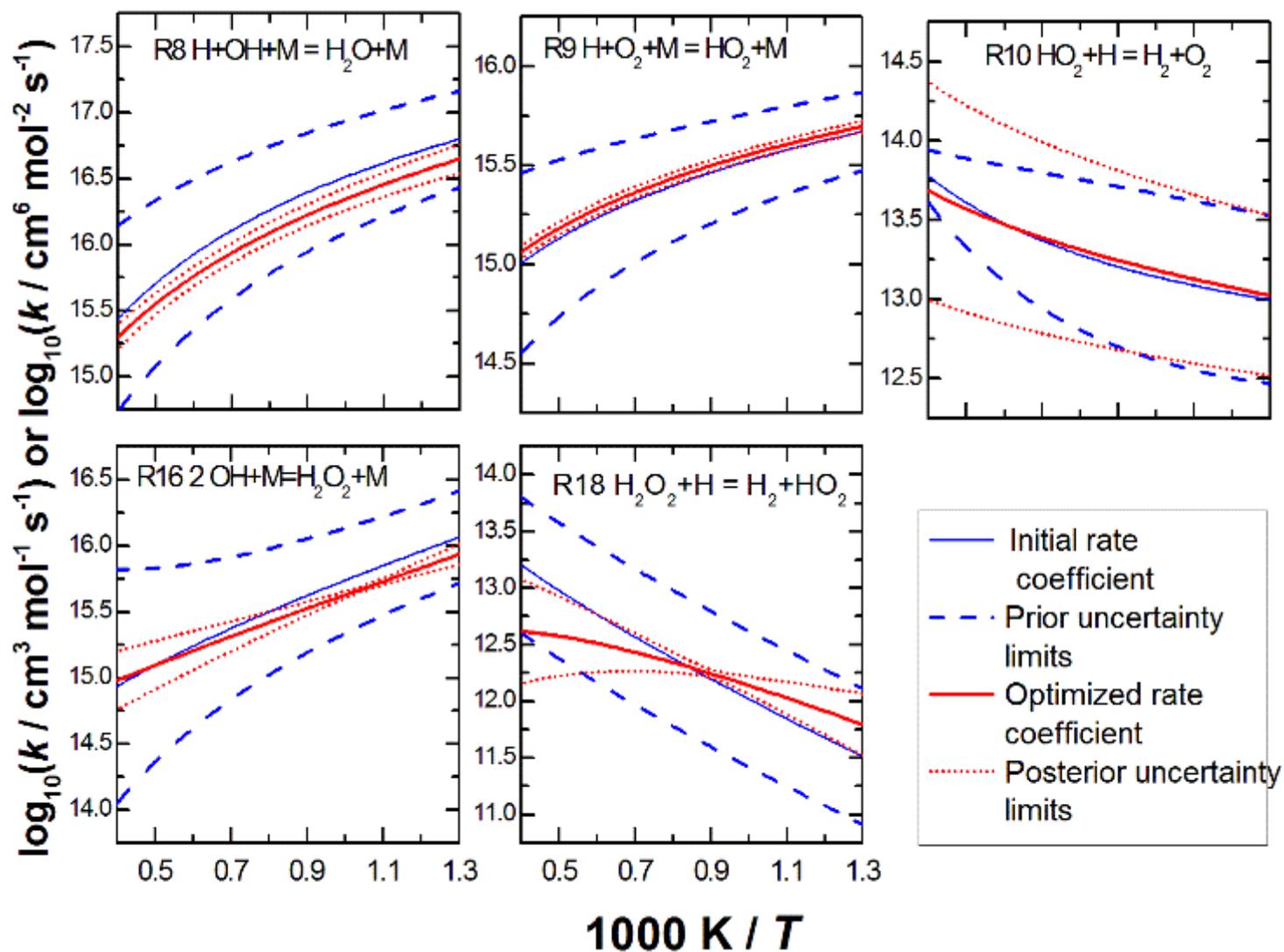
# Error function values for the initial and optimized mechanism



Measurement type	Kéromnès mechanism	Optimized mechanism
Shock tube	1.081	1.043
RCM	1.400	0.600
Burning velocities	3.115	1.770
Direct measurements	2.254	0.924
Total	7.851	4.338



# Estimated posterior rate coefficient uncertainties





# Results of optimization

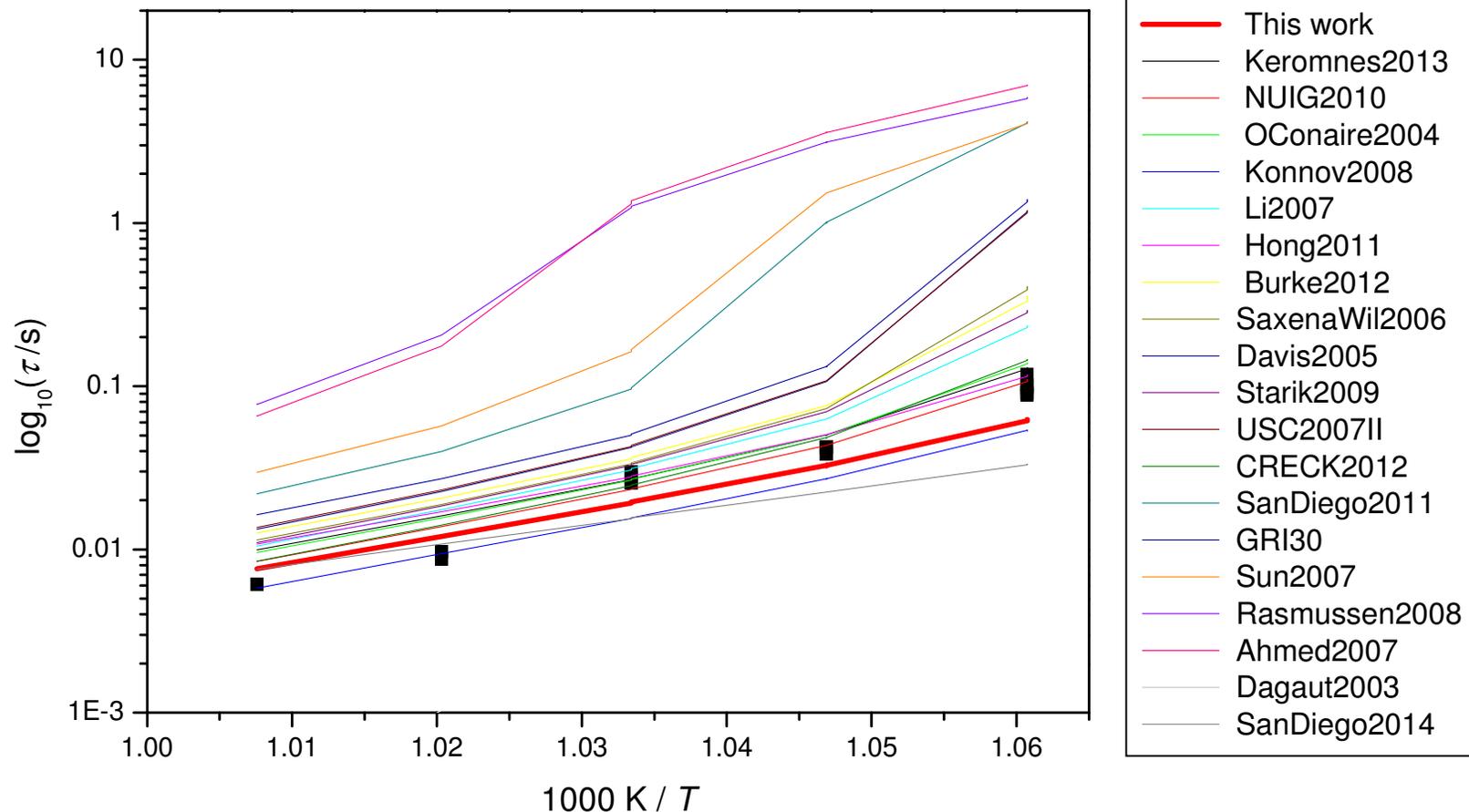
- **The optimized hydrogen combustion model**
  - Better overall performance than any previously published models
- **Set of optimized rate parameters**
  - 30 Arrhenius parameters and 3 third body collision efficiency parameters of 11 reactions
  - Can be considered our overall best knowledge of these rate coefficients
- **Posterior covariance matrix of the optimized parameters**
  - Temperature independent
  - Uncertainty (i.e. estimated scatter) of each optimized parameter
  - Correlation coefficients between the parameter pairs



# Testing the optimized mechanism



RCM study of Kéromnès *et al.* (2013)



## Experiments:

Kéromnès *et al.* *Combust. Flame*, **160**, 995-1011 (2013)

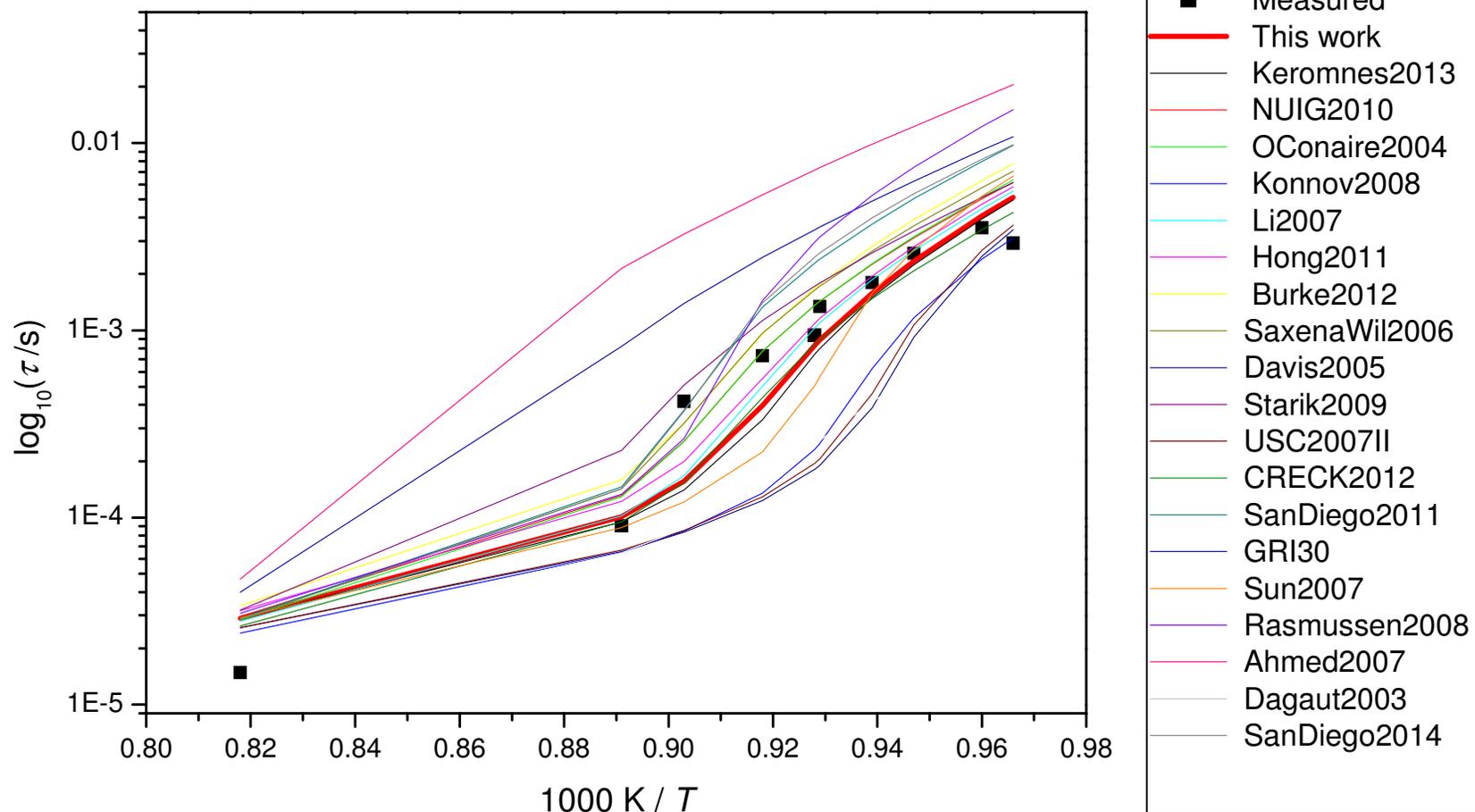
$p_{0,c} = 16$  bar equivalence ratio= 0.5



# Testing the optimized mechanism



Shock tube study of Zhang *et al.* (2012)



**Experiments:**

Zhang *et al.* *Combust. Flame*, **159**, 918-931 (2012)

$p_{0,c} = 10$  bar equivalence ratio= 0.5



# Comparison with other mechanisms

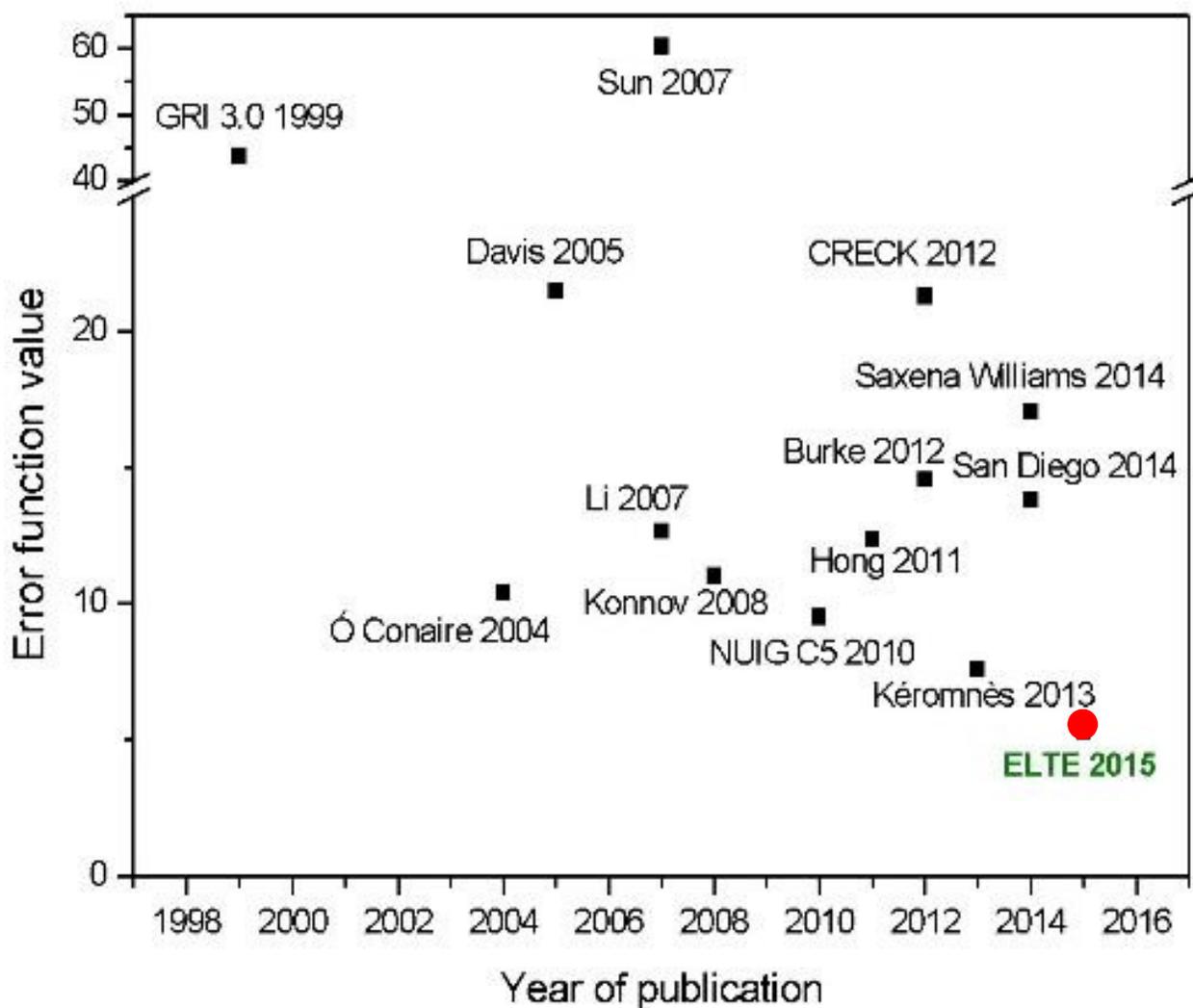


Error function values calculated for each mechanism, by experiment type

Mechanism	Error function values						Total (w/o He)	Total
	Shock tube	RCM	JSR	Flow reactors	Flames	Flames (w/o He)		
<b>Optimized mechanism</b>	5.94	6.70	2.97	8.08	4.86	6.11	<b>5.32</b>	<b>4.96</b>
<b>Kéromnès 2013</b>	6.69	11.33	3.02	13.25	8.11	5.88	<b>7.62</b>	<b>8.29</b>
<b>NUIG NGM 2010</b>	7.92	17.08	3.00	7.27	7.24	9.94	<b>9.53</b>	<b>8.45</b>
<b>Ó Conaire 2004</b>	8.51	23.15	2.96	8.18	-	8.90	<b>10.44</b>	-
<b>Konnov 2008</b>	9.67	27.61	3.06	10.91	-	6.37	<b>11.04</b>	-
<b>Hong 2011</b>	11.45	9.15	3.01	8.15	-	18.72	<b>12.40</b>	-
<b>Li 2007</b>	7.58	43.98	2.99	7.83	7.61	7.07	<b>12.69</b>	<b>12.04</b>
<b>Burke 2012</b>	13.29	48.54	3.06	3.91	4.57	5.91	<b>14.57</b>	<b>12.65</b>
<b>Saxena Williams 2006</b>	11.06	47.28	3.02	28.30	7.60	8.13	<b>17.05</b>	<b>15.43</b>
<b>San Diego 2014</b>	16.80	17.75	3.00	14.90	25.22	17.62	<b>13.86</b>	<b>17.22</b>
<b>CRECK 2012</b>	6.61	28.42	2.93	21.44	25.49	38.30	<b>21.32</b>	<b>18.58</b>
<b>Davis 2005</b>	11.62	93.55	3.00	4.89	5.84	7.58	<b>21.52</b>	<b>18.60</b>
<b>GRI 3.0 1999</b>	49.07	115.6	2.42	11.56	-	23.97	<b>43.78</b>	-
<b>Sun 2007</b>	11.99	309.2	3.11	25.42	15.31	18.60	<b>60.50</b>	<b>52.55</b>
<b>No. of data points</b>	566	219	149	191	432	319	<b>1390</b>	<b>1513</b>
<b>No. of data sets</b>	43	19	9	14	62	39	<b>121</b>	<b>145</b>



# Comparison with other mechanisms





# Related practical sessions

Monday 1-1 (Valkó)

Calculation of the prior uncertainty of rate coefficients  
*u-Limits*, UBAC, JPDAP and SAMAP

Wednesday 3-2 (Olm)

Validation of detailed combustion mechanisms  
outgen, Optima++

Thursday 4-1 (Varga)

Encoding combustion experimental data  
Optima++

Thursday 4-2 (Varga)

Optimization of detailed combustion mechanisms  
Optima++



# Have a good lunch!



Carsten Olm   Róbert Pálvölgyi   Tamás Varga  
Gergely Vincze   Tamás Turányi   Éva Valkó   István Gy. Zsély

## Financial support:

- ERA Chemistry grant (NN100523)
- OTKA grants (K84054 and K116117)

