

Determination of the joint uncertainty domain of rate parameters: The case study of hydrogen combustion



T. Turányi, T. Nagy, I.Gy. Zsély, T. Varga,
R. Pálvölgyi, I. Sedyó, C. Olm, H. J. Curran

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

Uncertainty of rate coefficients

Definition of uncertainty factor f :

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

Calculation of the variance of $\ln k$ from uncertainty factor f
(assuming 3σ deviation between $\ln k^0$ and $\ln k^{\max}$):

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

The databases of evaluated combustion kinetic rate parameters
e.g. Baulch *et al.*, 2005

- recommended temperature independent (constant) uncertainty
(usually selected from values $f = 0.1, 0.3, 0.5, 0.7, \text{ and } 1.0$)

OR

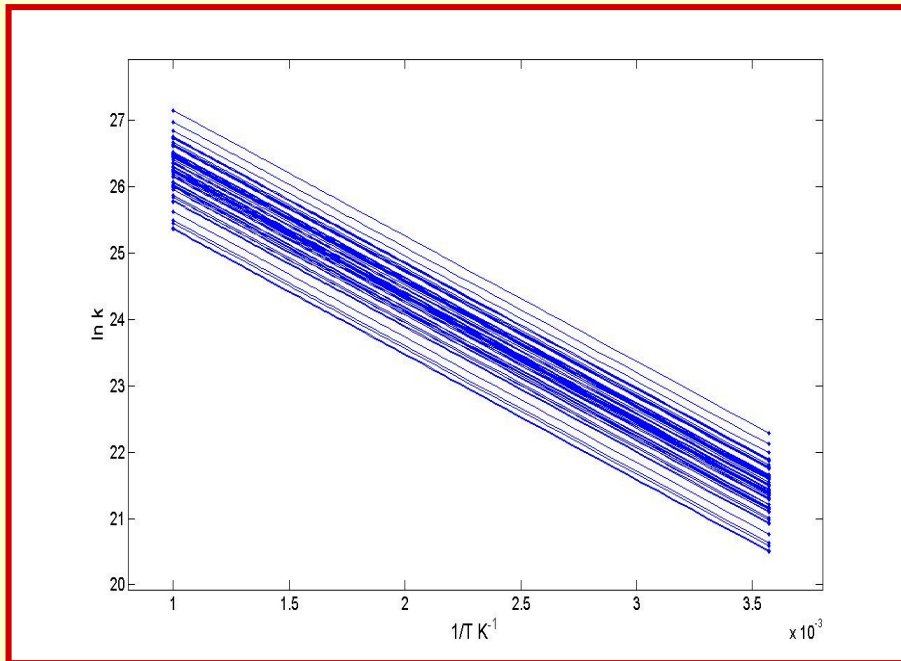
- uncertainty is defined at some temperatures (or temperature intervals)

Uncertainty parameter f in the databases

Features of uncertainty factor f :

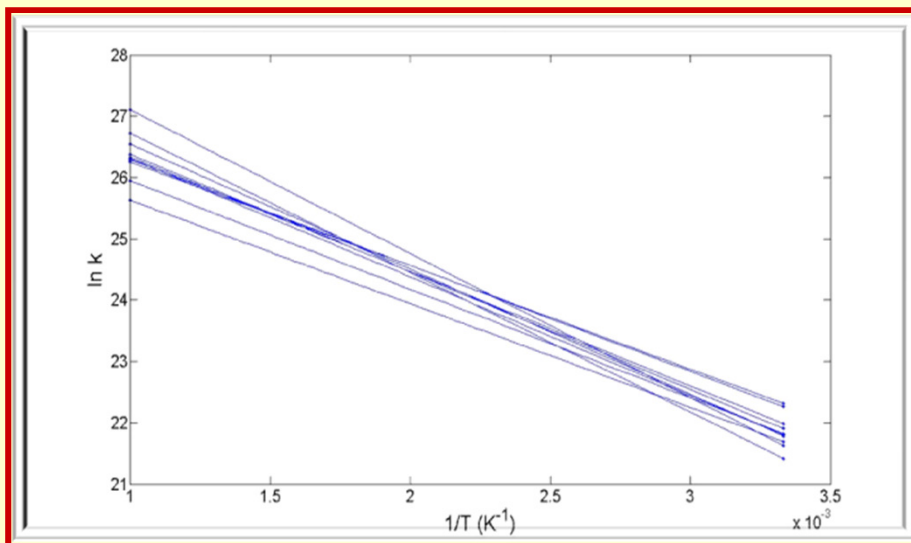
- widely used in the data collections / data evaluations (Warnatz, Tsang, Konnov, Baulch, NIST)
- available for most reactions
- some uncertainty analysis works have used it
- important input information in the mechanism optimization works of Frenklach *et al.* and Wang *et al.*
- no statistical background, subjective assessment
- Usually reflects a wider uncertainty than the quoted experimental uncertainty of the "best" measurement
- temperature dependence:
 - quoted to be temperature independent (50%)
 - defined at several (2-3) temperatures (50%)

Arrhenius plot ($\ln k$ vs. $1/T$) with uncertain parameter A :



**uncertainty of
⇒ the rate coefficient
is independent
of temperature**

Arrhenius plot ($\ln k$ vs. $1/T$) with uncertain parameters A and E :



**uncertainty of
⇒ the rate coefficient
depends
on temperature**

extended Arrhenius expression:

$$k(T) = AT^n \exp(-E/RT)$$

linearized form:

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

- Matrix-vector form of the linearized Arrhenius equation:

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

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

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

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

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

$$\sigma_\kappa(\theta) = \sqrt{\boldsymbol{\theta}^T \boldsymbol{\Sigma}_p \boldsymbol{\theta}}$$

⇒ the temperature dependent standard deviation of k can be calculated from a quadratic form.

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

- For the 3-parameter Arrhenius equation

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

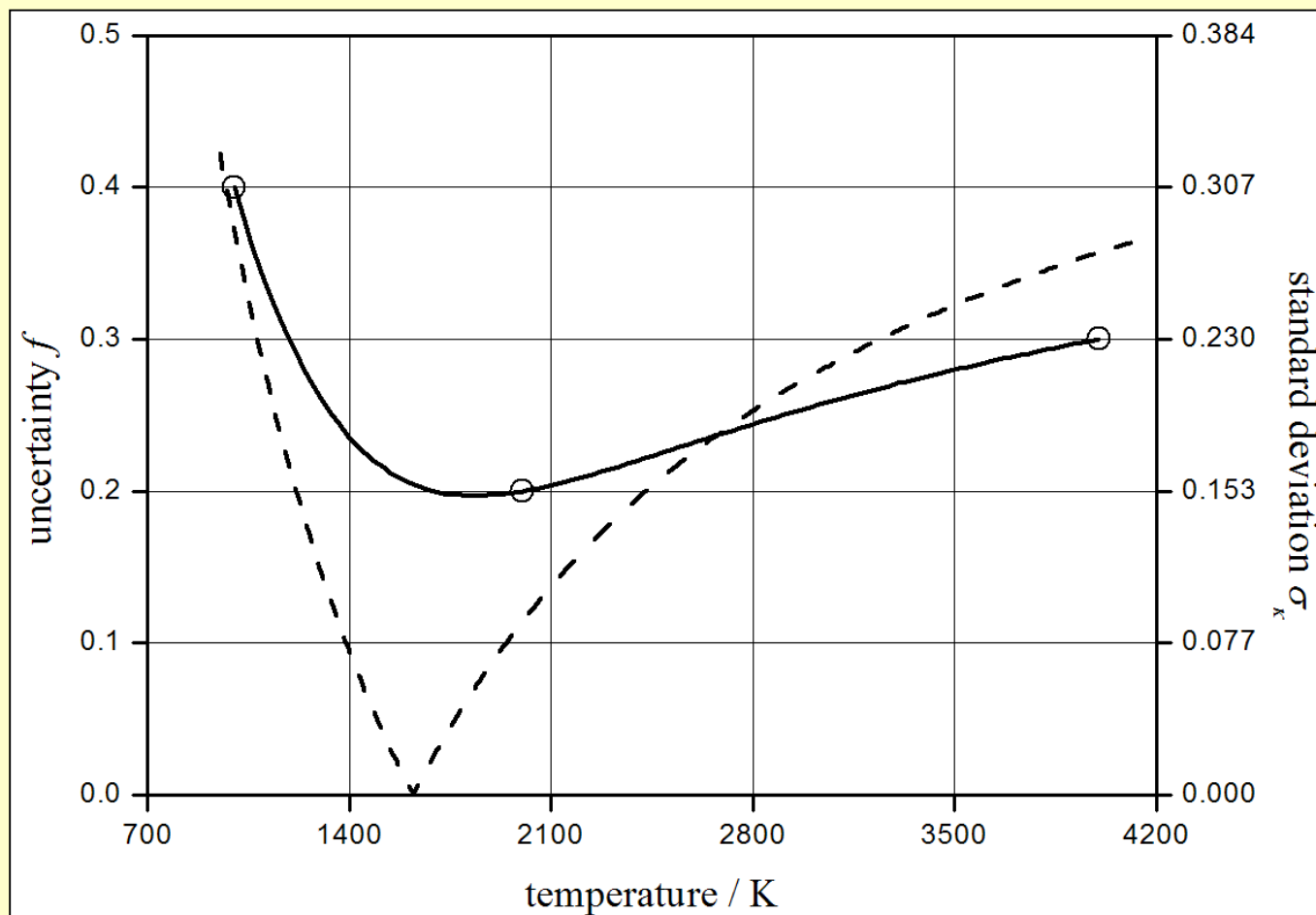
- For the original (2-parameter) Arrhenius equation:

$$\sigma_k(\theta) = \sqrt{\sigma_\alpha^2 + \sigma_\varepsilon^2 \theta^{-2} - 2r_{\alpha\varepsilon} \sigma_\alpha \sigma_\varepsilon \theta^{-1}}$$

- ⇒ If the variance of k is known at several (at least 6) temperatures the covariance matrix of the Arrhenius parameters can be calculated
- ⇒ The uncertainty limits of the Arrhenius parameters can be determined.
- ⇒ If $\ln k$ has normal distribution \Leftrightarrow the Arrhenius parameters have joint multivariate normal distribution.

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

temperature dependence of the uncertainty of the rate coefficient (1000K–4000K)



$$k(T) = A \exp(-E/RT)$$

$$\kappa(\theta) = \alpha - \varepsilon \cdot \theta^{-1}$$

$$\bar{\alpha} = 32,134$$

$$\bar{\varepsilon} = 13930$$

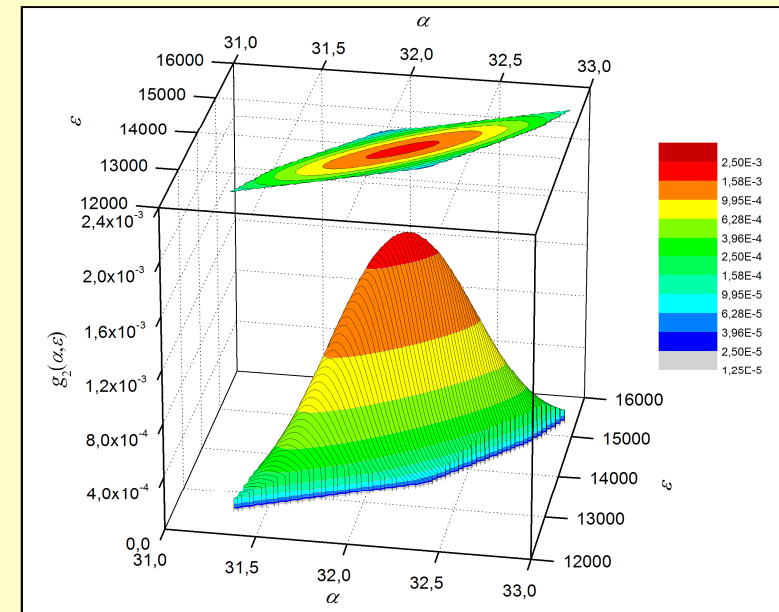
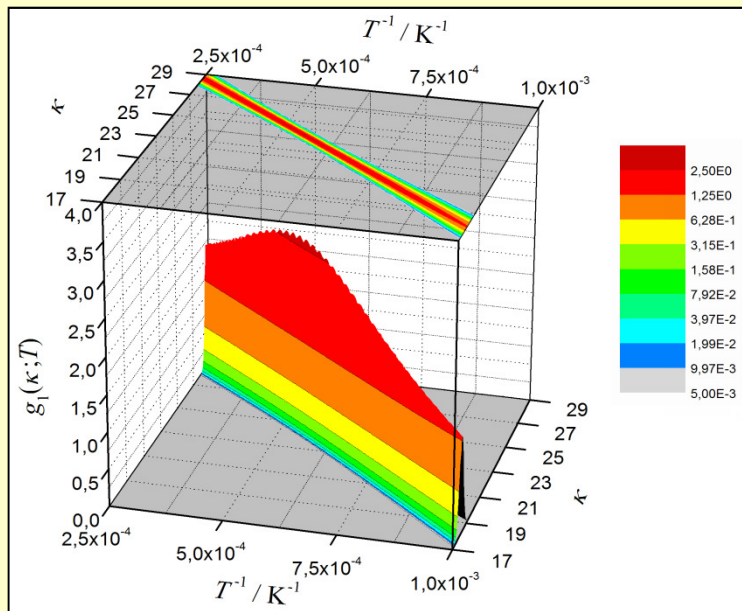
$$\sigma_{\alpha} = 0,355$$

$$\sigma_{\varepsilon} = 588$$

$$r_{\alpha\varepsilon} = 0,9045$$

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

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



**Temperature dependent
1D normal
probability density function (*pdf*)
of the rate coefficient
(1000 K – 4000 K)**

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

Estimation of the temperature dependent uncertainty

For most of the reactions the data evaluations define

- temperature independent f (constant $f(T)$ function)

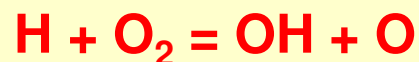
OR

- a verbally defined $f(T)$ function

" $f = 0.1$ at 800 K raising to 0.2 at 2000 K "

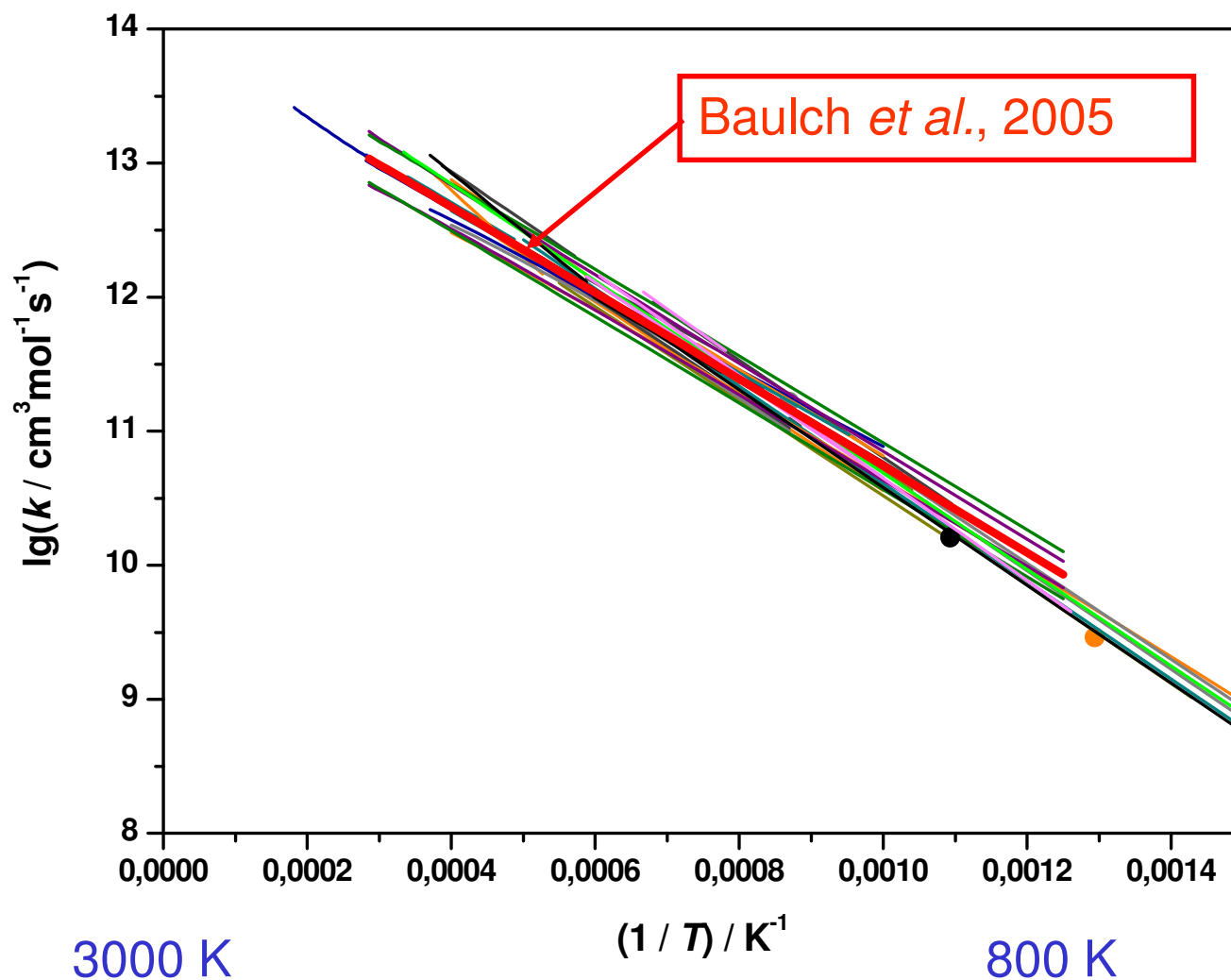
Reassessment of the $f(T)$ functions is needed!

Example:

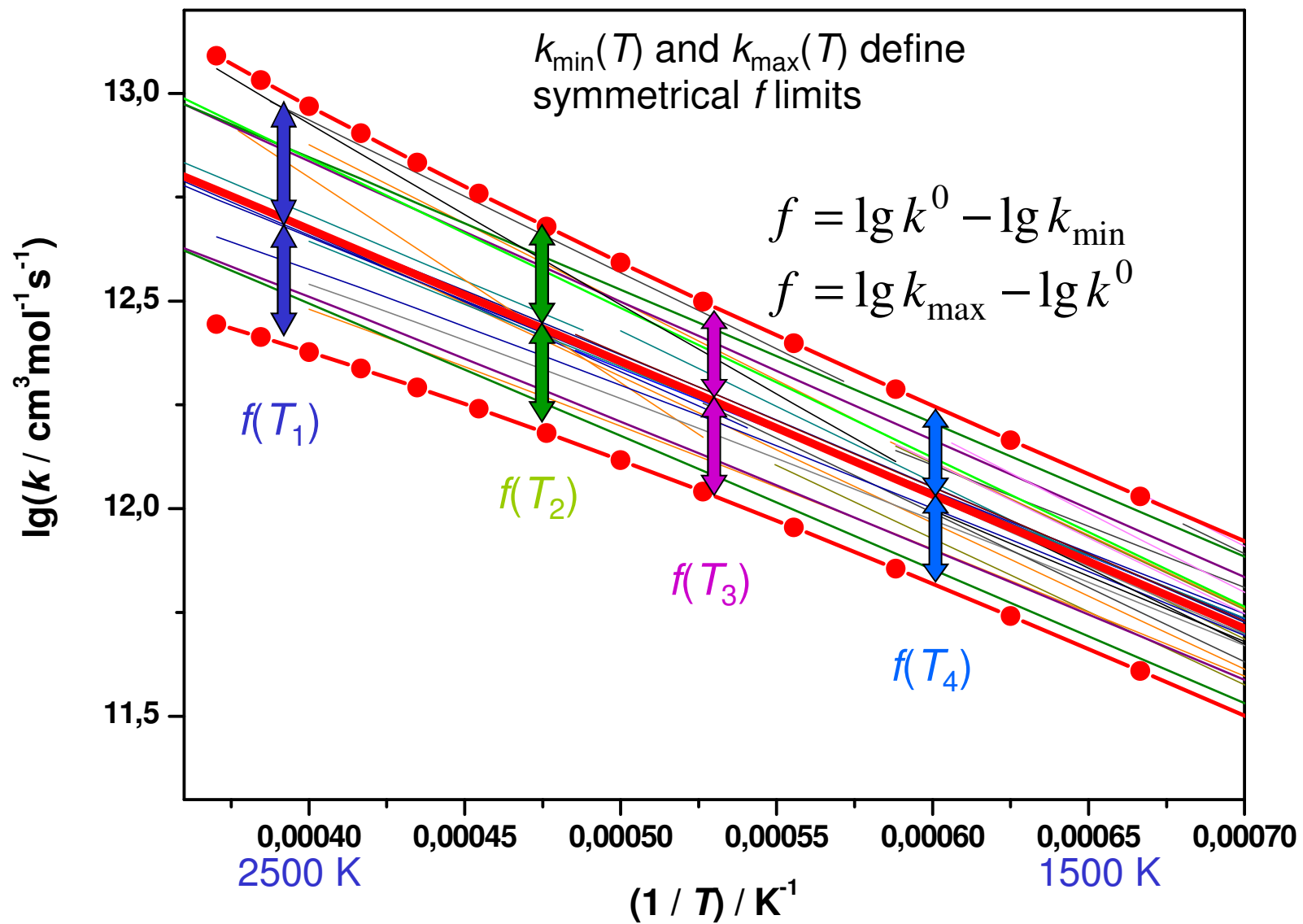


Reaction $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$

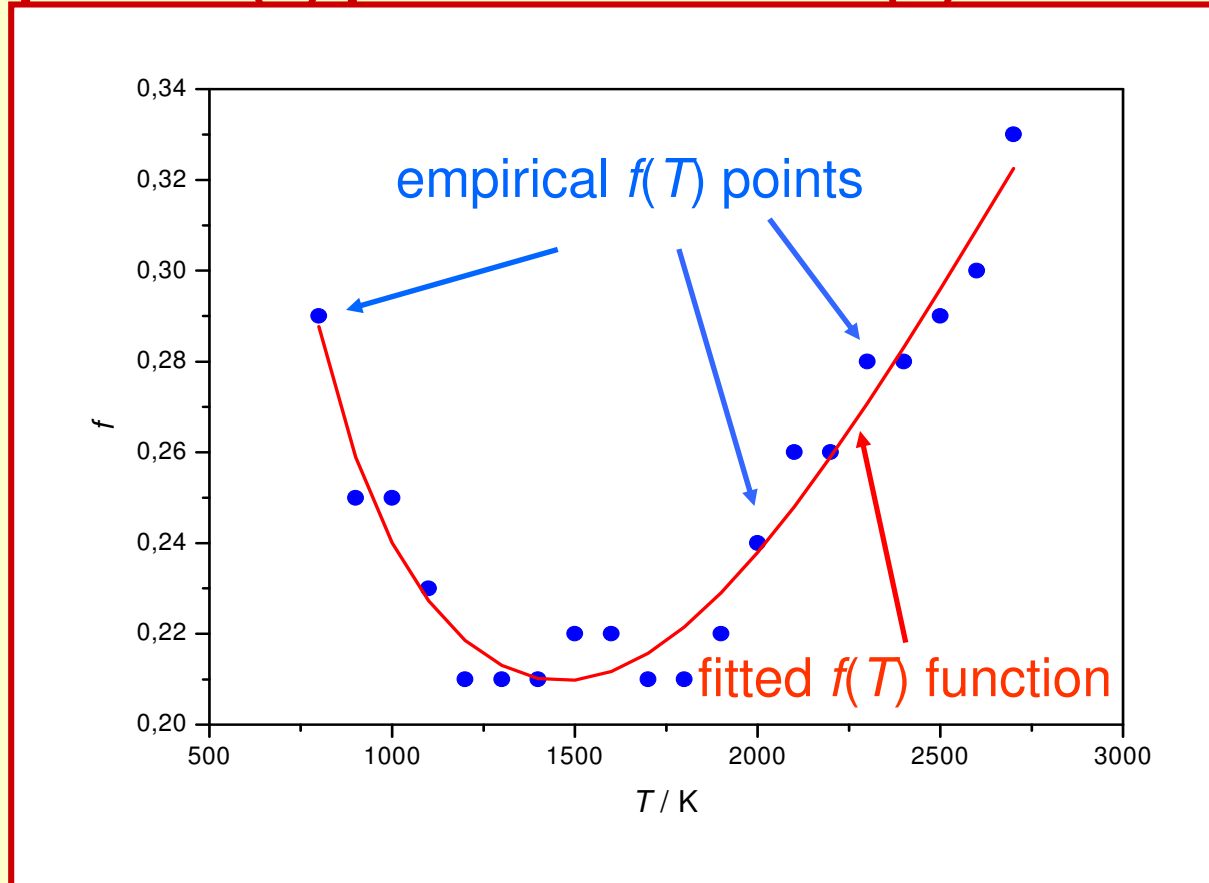
All experimental and theoretical (TST) results from the NIST database



Definition of k_{\min} and k_{\max} ranges of uncertainty



Empirical $f(T)$ points and fitted $f(T)$ function



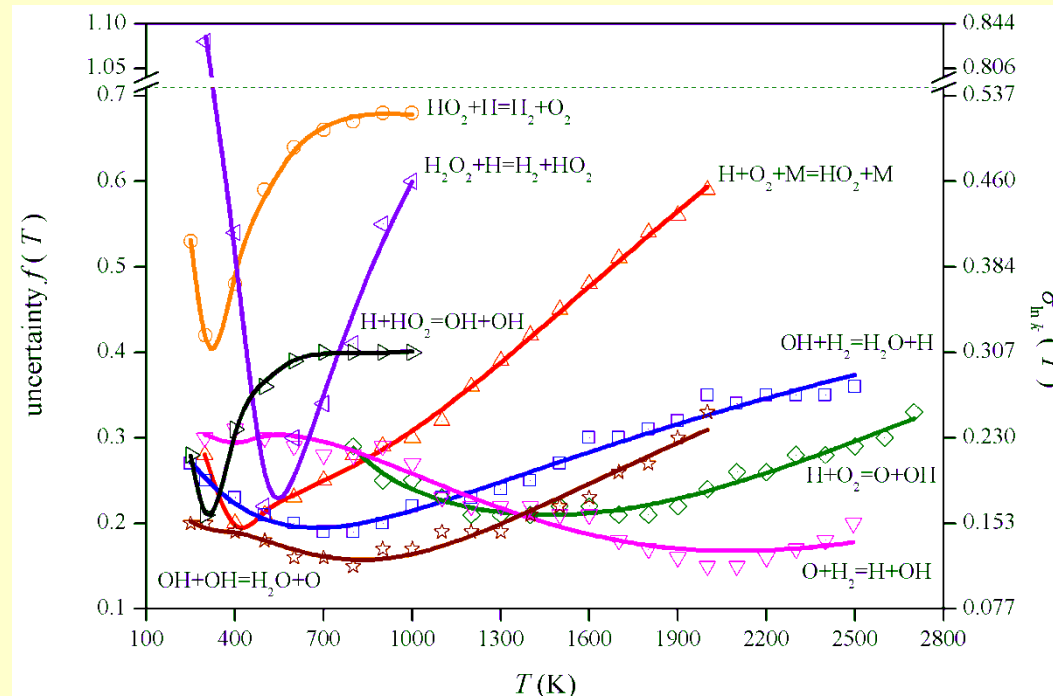
$$f(T) = \frac{3}{\ln 10} \sqrt{\sigma_{\alpha}^2 + \sigma_{\varepsilon}^2 T^{-2} + \sigma_n^2 \ln^2 T - 2r_{\alpha\varepsilon} \sigma_{\alpha} \sigma_{\varepsilon} T^{-1} - 2r_{\varepsilon n} \sigma_{\varepsilon} \sigma_n T^{-1} \ln T + 2r_{\alpha n} \sigma_{\alpha} \sigma_n \ln T}$$

Nagy, T.; Turányi, T.

Uncertainty of Arrhenius parameters

Int. J. Chem. Kinet., **43**, 359-378(2011)

Temperature dependence of the uncertainty of the rate coefficients of the most important H/O reactions



The procedure above was repeated for several H/O reactions

Sedyó, I; Nagy, T; Zsély, I; Turányi, T

Uncertainty of the Arrhenius parameters of important elementary reactions of the hydrogen-oxygen system

Proceedings of the ECM, 2011

Comprehensive determination of the uncertainty of the rate parameters

Required features

1. The determination should take into account all available information:

Direct measurements: determination of the rate coefficient of a single reaction step at given temperature, pressure and bath gas

Indirect measurements: ignition delay time, laminar flame velocity, measured concentration profiles

Theoretical calculations / estimations: uncertainty is critical

2. Statistics based (reproducible) definition of the uncertainty

3. Joint uncertainty for all rate parameters:

Arrhenius parameters A , n , E for each reaction step,
3rd body efficiencies, parameters of pressure dependence

4. Extensions:

thermodynamic data: in accordance with the ATcT method

other parameters of simulations: e.g. transport data

Step 1: Collection of large amount of indirect measurements

Aim: collection of all direct and indirect measurement, ever measured, related to hydrogen combustion

Reality: pre-selection was needed, many obsolete measurements (before about 1950) were not considered

- **ignition delay time measurements in shock tubes:** 796 data points in 55 data series from 17 publications
- **ignition delay time measurements in rapid compression machines (RCMs):** 623 data points in 44 data series from one publication
- **Laminar flame velocity measurements:** 622 data points in 64 data series from 23 publications
- **concentrations measured in PSRs:** 152 data points in 9 data series from one publication
- **concentration–distance profiles in turbulent flow reactors:** 214 data points in 16 data series from one publication

Total: 2407 data points in 188 data series from 43 publications.

All experimental data were encoded in PRIME XML data format.

PrIMe database

PrIMe (Process Informatics Model) database of Michael Frenklach:

www.primekinetics.org

Open database that contains the description of several hundred indirect combustion measurements.

Special XML data format:

defines all experimental conditions and measurement data.

We have created computer codes for

- encoding literature data OR other experimental data in PrIMe XML format
- carrying out simulations based on a PrIMe datafile (ignition in shock tube, laminar stationary flame, tubular reactor)
- calculating the deviations between the experimental and simulated data

PrIME-format encoding of a shock tube experiment

```
<commonProperties>
  <property description="pressure behind reflected shock waves"
    label="P5" name="pressure" units="atm">
    <value>64</value>
    <uncertainty bound="plusminus" kind="relative"
      transformation="1">0.01</uncertainty>
  </property>
  <property name="initial composition">
    <component>
      <speciesLink preferredKey="H2" primeID="s00009809" />
      <amount units="mole fraction">0.0033</amount>
    </component>
    <component>
      <speciesLink preferredKey="O2" primeID="s00010295" />
      <amount units="mole fraction">0.00167</amount>
    </component>
    <component>
      <speciesLink preferredKey="Ar" primeID="s00000049" />
      <amount units="mole fraction">0.99503</amount>
    </component>
  </property>
</commonProperties>
```

Step 2: Cross testing of mechanisms vs. data

Mechanisms:

Group 1: hydrogen combustion mechanisms

- **Ó Conaire 2004:** 10 species, 21 reactions
Ó Conaire, M.; Curran, H. J.; Simmie, J. M.; Pitz, W. J.; Westbrook, C. K. *Int. J. Chem. Kinet.* **2004**, **36**, 603-622.
- **Konnov 2008:** 10 species, 33 reactions
Konnov, A. A. *Combust. Flame* **2008**, **152**, 507-528.
- **Hong 2011:** 10 species, 31 reactions
Hong, Z.; Davidson, D. F.; Hanson, R. K. *Combust. Flame* **2011**, **158**, 633-644.
- **Burke 2012:** 11 species, 27 reactions
Burke, M. P.; Chaos, M.; Ju, Y.; Dryer, F. L.; Klippenstein, S. J. *Int. J. Chem. Kinet.* **2012**, **44**, 444-474.

Group 2: originally developed for wet CO combustion

- **Zsély 2005:** 10 species, 32 reactions
Zsély, I. G.; Zádor, J.; Turányi, T. *Proc. Combust. Instit.* **2005**, **30/1**, 1273-1281.
- **Sun 2007:** 11 species, 32 reactions
H. Sun, S.I. Yang, G. Jomaas, C.K. Law, *Proc. Comb. Inst.* **2007**, **31**, 439-446.
- **CRECK 2012:** 11 species, 21 reactions
Frassoldati, A.; Ranzi, E.; Faravelli, T. CRECK modeling Group Hydrogen/CO mechanism version 1201.
<http://creckmodeling.chem.polimi.it/kinetic.html>
- **Rasmussen 2008:** 10 species, 30 reactions
C. L. Rasmussen; J. Hansen; P. Marshall; P. Glarborg, *Int. J. Chem. Kinet.* **2008**, **40**, 454-480.
- **Keromnes 2012:** 12 species, 33 reactions
A. Keromnes, 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* (submitted)

Group 3: originally developed for hydrocarbon combustion

- **GRI 3.0:** 10 species, 29 reactions
Smith, G P; Golden, D M; Frenklach, M; Moriarty, N W; Eiteneer, B; Goldenberg, M; Bowman, C T; Hanson, R K; Song, S; Gardiner, W C; Lissianski, V V; Qin, Z GRI-Mech 3.0 http://www.me.berkeley.edu/gri_mech/23/11/2011/
- **Li 2007:** 11 species, 25 reactions
Li, J.; Zhao, Z.; Kazakov, A.; Chaos, M.; Dryer, F. L.; Scire, J. J. *Int. J. Chem. Kinet.* **2007**, **39**, 109-136.
- **USC 2007:** 10 species, 28 reactions
H. Wang; X. You; A. V. Joshi; S. G. Davis; A. Laskin; F. Egolfopoulos; C. K. Law USC Mech Version II.
High-Temperature Combustion Reaction Model of H₂/CO/C₁-C₄ Compounds. http://ignis.usc.edu/USC_Mech_II.htm
(May 2007)
- **San Diego 2011:** 11 species, 21 reactions
San Diego Mechanism, version 2011-11-22. <http://combustion.ucsd.edu>

Comparison of experimental data and simulation results

Objective function Q :

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

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

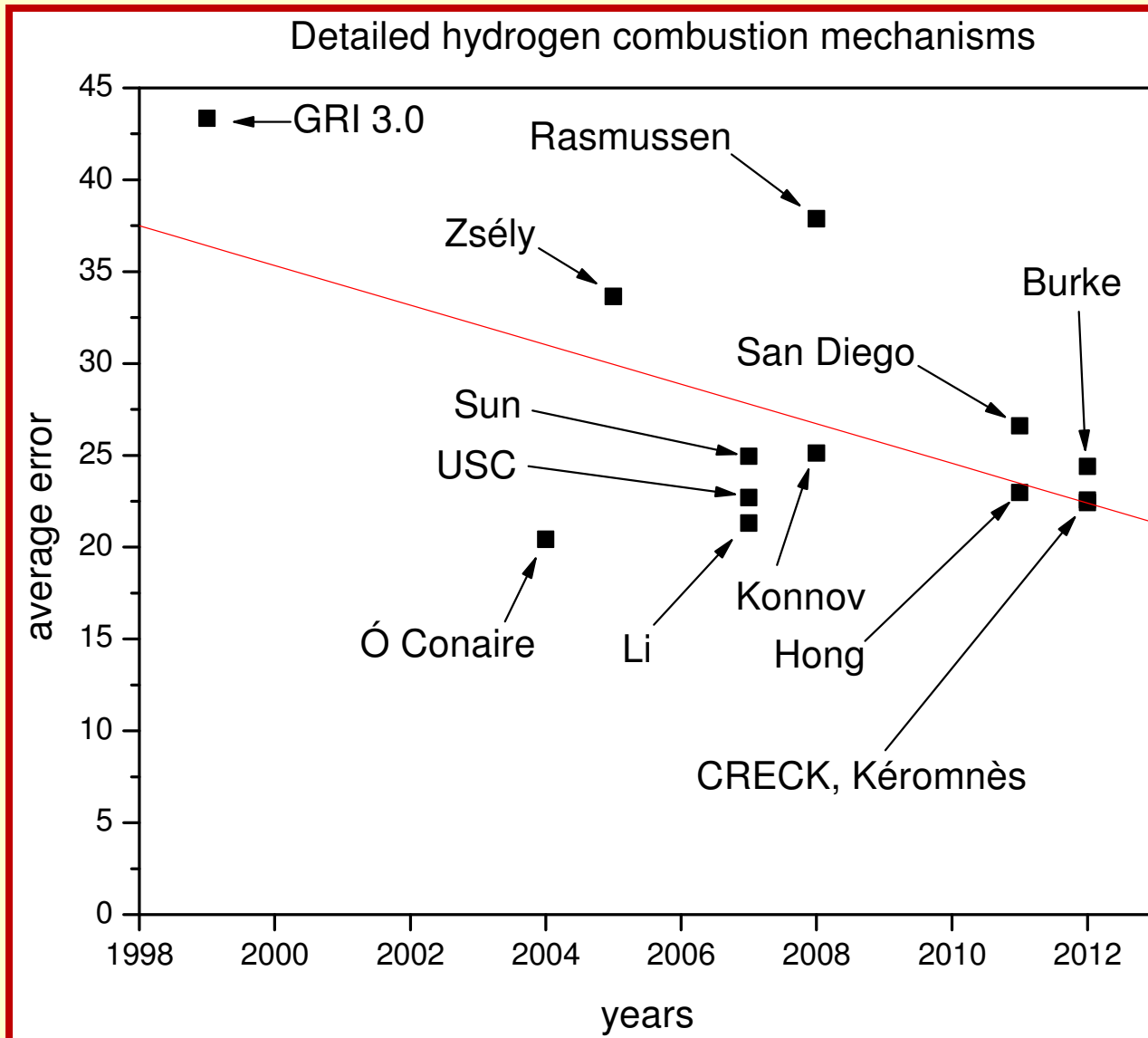
y_{ij} measured/calculated rate coefficient OR
measured/calculated ignition time/flame velocity
in data point j of data series i

σ standard deviation of the measured data

N_i number of data points in data series i

N number of data series (different experiments)

Performance of the mechanisms vs. years



Results of cross testing

Ignition delays	average of error function values			Mechanism	Asaba <i>et al.</i> (1965) only
	PSR	flame	Overall performance		
48.13	26.34	32.67	43.34	GRI 3.0 1999	184.31
13.89	49.40	30.80	20.42	Ó Conaire 2004	122.88
21.87	83.19	54.34	33.64	Zsély 2005	143.30
14.00	54.57	32.32	21.31	Li 2007	154.69
17.87	65.83	29.27	24.94	Sun 2007	159.96
16.33	51.98	32.06	22.70	USC 2007 Version II	161.65
15.12	82.59	31.52	25.12	Konnov 2008	153.68
31.55	82.11	36.14	37.87	Rasmussen 2008	152.07
16.80	54.48	29.78	22.97	Hong 2011	165.11
20.77	55.60	33.65	26.61	San Diego 2011	181.05
18.69	52.15	31.66	24.39	Burke 2012	171.97
11.88	57.08	48.03	22.43	CRECK 2012	157.02
14.39	65.39	30.74	22.56	Kéromnès 2012	163.74
634	136	200	970	No. data points	37
53	8	19	80	No. datasets	3

Some indirect experimental data series are presumably wrong and these were excluded from the optimization and mechanism testing.

example: T. Asaba, W.C. Gardiner, R.F. Stubbelman,
Proc. Combust. Inst., **10**, 295-302(1965)

Step 3: Optimization of the rate parameters

1. **Direct and indirect measurements** are taken into account **simultaneously**.
2. The **uncertainty domain of all the Arrhenius parameters** is determined
3. For each important reaction step, the Arrhenius parameters **A , n , E** and maybe other rate parameters are determined within their domain of uncertainty.

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

Optimization and uncertainty estimation of parameters

Optimization = minimization of this error function:

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

y_k measured/calculated rate coefficient **OR**
measured/simulated indirect measurement

Calculation of the covariance matrix of the estimated parameters:

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

Transformation of the covariance matrix of parameters to „traditional” gas kinetics measures of uncertainty

covariance matrix of Arrhenius parameters \rightarrow covariance matrix of $\ln k$

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

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

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

covariance matrix of $\ln k \rightarrow$ correlation r between the $\ln k$ values

$$r_{\kappa_i, \kappa_j}(T) = \frac{\text{cov}(\kappa_i(T), \kappa_j(T))}{\sigma_{\kappa_i}(T) \sigma_{\kappa_j}(T)}$$

Strategy for optimization

STEP1

STEP2

STEP3

experiment	number of datapoints	H+O2=O+OH	LPH+O2(+M)=HO2(+M)	O+H2=H+OH	OH+H2=H+H2O	H2O2+H=H2+HO2	HO2+H=2OH	HO2+H=H2+O2	HO2+OH<=>H2O+O2
Herzler et al. (2009 ^a)	9	○	○						
Fujimoto and Suzuki (1967)	9	○	○						
Zhang et. al. (2012 ^a)	7	○	○						
Naumann et. al. (2011 ^a)	19	○	○						
Naumann et. al. (2011 ^b)	26	○	○						
Petersen et al. (2003 ^a)	9	○		○					
Cheng and Oppenheim (1984 ^a)	58	○		○					
Petersen et al. (2003 ^b)	24	○		○					
Petersen et al. (2003 ^c)	4	○		○					
Petersen et al. (1996 ^a)	16	○	○	○					
Petersen et al. (1996 ^b)	6	○	○	○					
Slack (1977)	12	○	○	○					
Bhaskaran et al. (1973)	14	○	○	○					
Wang et al. (2003 ^a)	12	○	○	○					
Naumann et. al. (2011 ^c)	13	○	○	○					
Chaumeix et al. (2007 ^a)	5	○		○	○				
Chaumeix et al. (2007 ^b)	7	○		○	○	○			
Chaumeix et al. (2007 ^c)	5	○		○	○	○			
Cohen et. al. (1967)	21	○		○	○	○			
Cheng and Oppenheim (1984 ^b)	56	○	○	○	○	○			
Naumann et. al. (2011 ^d)	19	○	○	○	○	○			
Naumann et. al. (2011 ^e)	19	○	○	○	○	○			

STEP 2

Petersen et al. (2003 ^a)	9	○		○
Cheng and Oppenheim (1984 ^a)	58	○		○
Petersen et al. (2003 ^b)	24	○		○
Petersen et al. (2003 ^c)	4	○		○
Petersen et al. (1996 ^a)	16	○	○	○
Petersen et al. (1996 ^b)	6	○	○	○
Slack (1977)	12	○	○	○
Bhaskaran et al. (1973)	14	○	○	○
Wang et al. (2003 ^a)	12	○	○	○
Naumann et. al. (2011 ^c)	13	○	○	○

STEP 3

Chaumeix et al. (2007 ^a)	5	○		○	○
Chaumeix et al. (2007 ^b)	7	○		○	○
Chaumeix et al. (2007 ^c)	5	○		○	○
Cohen et. al. (1967)	21	○		○	○
Cheng and Oppenheim (1984 ^b)	56	○	○	○	○
Naumann et. al. (2011 ^d)	19	○	○	○	○
Naumann et. al. (2011 ^e)	19	○	○	○	○

STEP 4

Zhang et. al. (2012 ^b)	10	○	○			○
Wang et al. (2003 ^b)	10	○	○			○
Wang et al. (2003 ^c)	21	○	○			○
Naumann et. al. (2011 ^f)	9	○	○	○		○

STEP 5

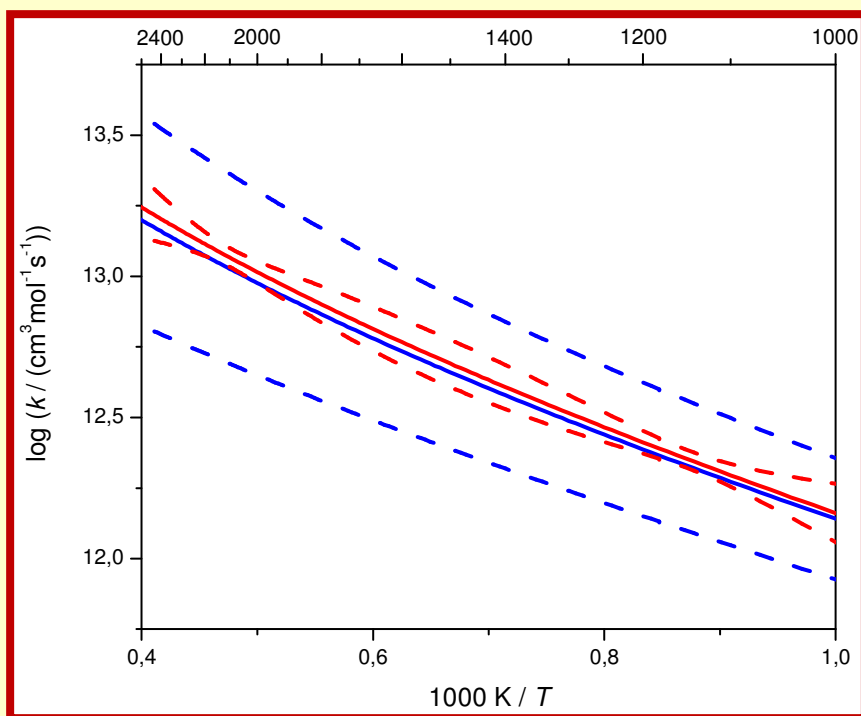
Wang et al. (2003 ^d)	12	○	○			○	○
Naumann et. al. (2011 ^g)	10	○	○			○	○
Petersen et al. (1996 ^c)	8	○	○			○	○
Herzler et al. (2009 ^b)	9	○	○			○	○
Petersen et al. (1996 ^d)	3	○	○		○	○	○
Zhang et. al. (2012 ^c)	8	○	○			○	○
Herzler et al. (2009 ^c)	12	○	○			○	○
Naumann et. al. (2011 ^h)	16	○	○			○	○

STEP 6

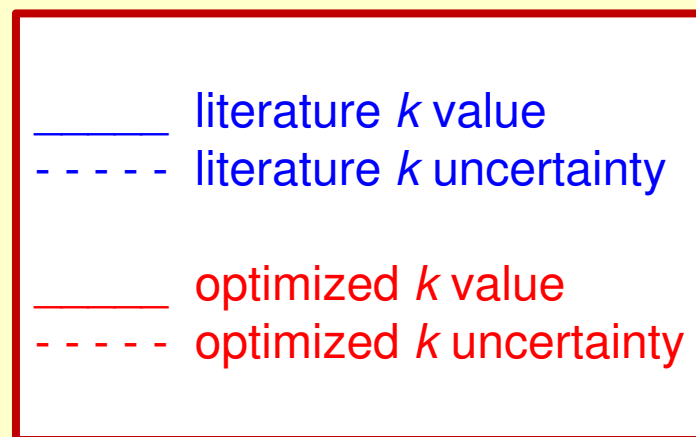
Petersen et al. (1996 ^e)	14	○		○				○	
Petersen et al. (1996 ^f)	7	○	○	○				○	
Schott and Kinsey (1958)	17	○		○	○			○	
Petersen et al. (1996 ^g)	17	○	○	○				○	
Naumann et. al. (2011 ⁱ)	18	○	○	○	○			○	
Naumann et. al. (2011 ^j)	13	○	○	○	○	○	○		○

Results of optimization

- A new set of optimized rate parameters
(in this case: 26 optimized parameters (23 Arrhenius parameters of 8 reactions
3 third body efficiencies))
- Covariance matrix of all optimized parameters
CONVERTED TO
- $f(T)$ uncertainty function for each rate coefficient
- $r(T)$ correlation function of pairs of rate coefficients

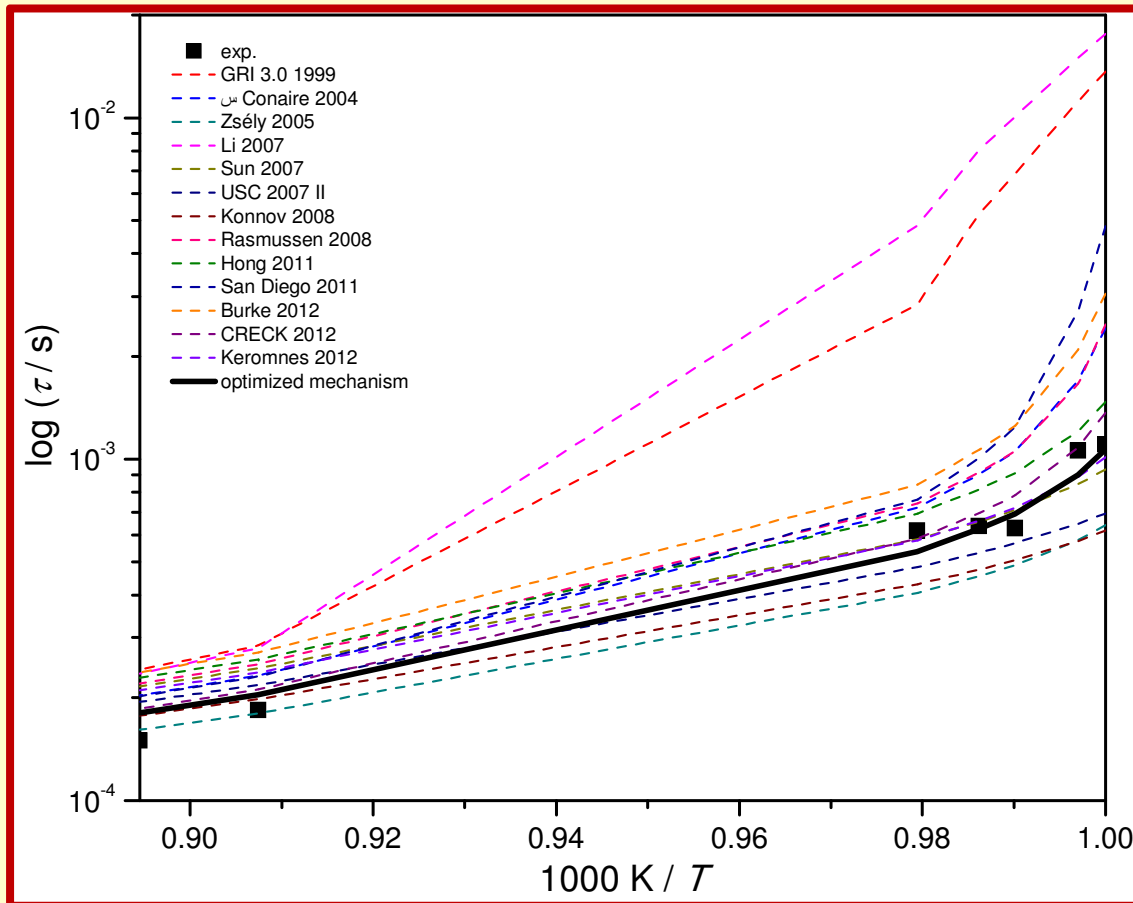


reaction $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$:



Step 4: Testing the optimized mechanism against other mechanisms

The optimization code created figures on the agreement of the simulation results and the experimental points.



experiments: Pang, G.A., Davison, D.F., Hanson, R.K.,
Proc. Combust. Inst., **32**, 181-188(2009)
Fig. 3., full square; 4% H₂ / 2% O₂ / Ar, P_{t=0} = 3.5 atm

Testing the optimized mechanism against other mechanisms

mechanisms	set #1		
GRI 3.0 1999	43.63		
Ó Conaire 2004	11.01		
Zsély 2005	16.64		
Li 2007	11.47		
Sun 2007	15.72		
USC 2007 II	14.31		
Konnov 2008	12.42		
Rasmussen 2008	28.58		
Hong 2011	14.44		
San Diego 2011	18.18		
Burke 2012	16.49		
CRECK 2012	9.28		
Kéromnès 2012	11.94		
optimized mechanism	8.25		

error function values (smaller is better)

set #1: Ignition time experiments *used at the optimization*

Testing the optimized mechanism against other mechanisms

mechanisms	set #1	set#2	
GRI 3.0 1999	43.63	48.13	
Ó Conaire 2004	11.01	13.89	
Zsély 2005	16.64	21.87	
Li 2007	11.47	14.00	
Sun 2007	15.72	17.87	
USC 2007 II	14.31	16.33	
Konnov 2008	12.42	15.12	
Rasmussen 2008	28.58	31.55	
Hong 2011	14.44	16.80	
San Diego 2011	18.18	20.77	
Burke 2012	16.49	18.69	
CRECK 2012	9.28	11.88	
Kéromnès 2012	11.94	14.39	
optimized mechanism	8.25	11.59	

set #1: Ignition time experiments *used at the optimization*

set #2: All available ignition time experiments

Testing the optimized mechanism against other mechanisms

mechanisms	set #1	set#2	set#3
GRI 3.0 1999	43.63	48.13	43.34
Ó Conaire 2004	11.01	13.89	20.42
Zsély 2005	16.64	21.87	33.64
Li 2007	11.47	14.00	21.31
Sun 2007	15.72	17.87	24.94
USC 2007 II	14.31	16.33	22.70
Konnov 2008	12.42	15.12	25.12
Rasmussen 2008	28.58	31.55	37.87
Hong 2011	14.44	16.80	22.97
San Diego 2011	18.18	20.77	26.61
Burke 2012	16.49	18.69	24.39
CRECK 2012	9.28	11.88	22.43
Kéromnès 2012	11.94	14.39	22.56
optimized mechanism	8.25	11.59	19.35

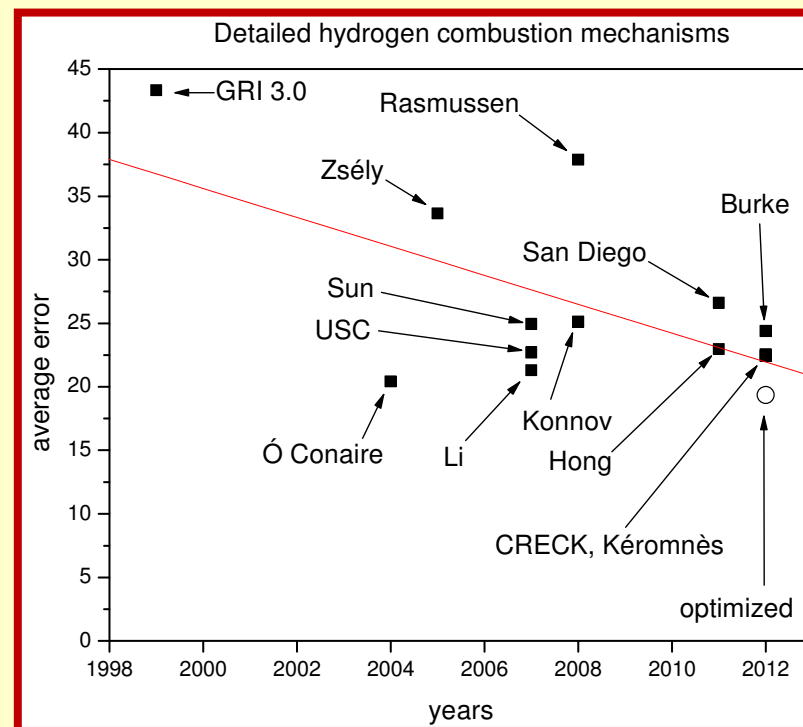
set #1: Ignition time experiments *used at the optimization*

set #2: All available ignition time experiments

set #3: All types of data (ignition time, PSR, laminar flame velocity)

Testing the optimized mechanism against other mechanisms

mechanisms	set #1	set#2	set#3
GRI 3.0 1999	43.63	48.13	43.34
Ó Conaire 2004	11.01	13.89	20.42
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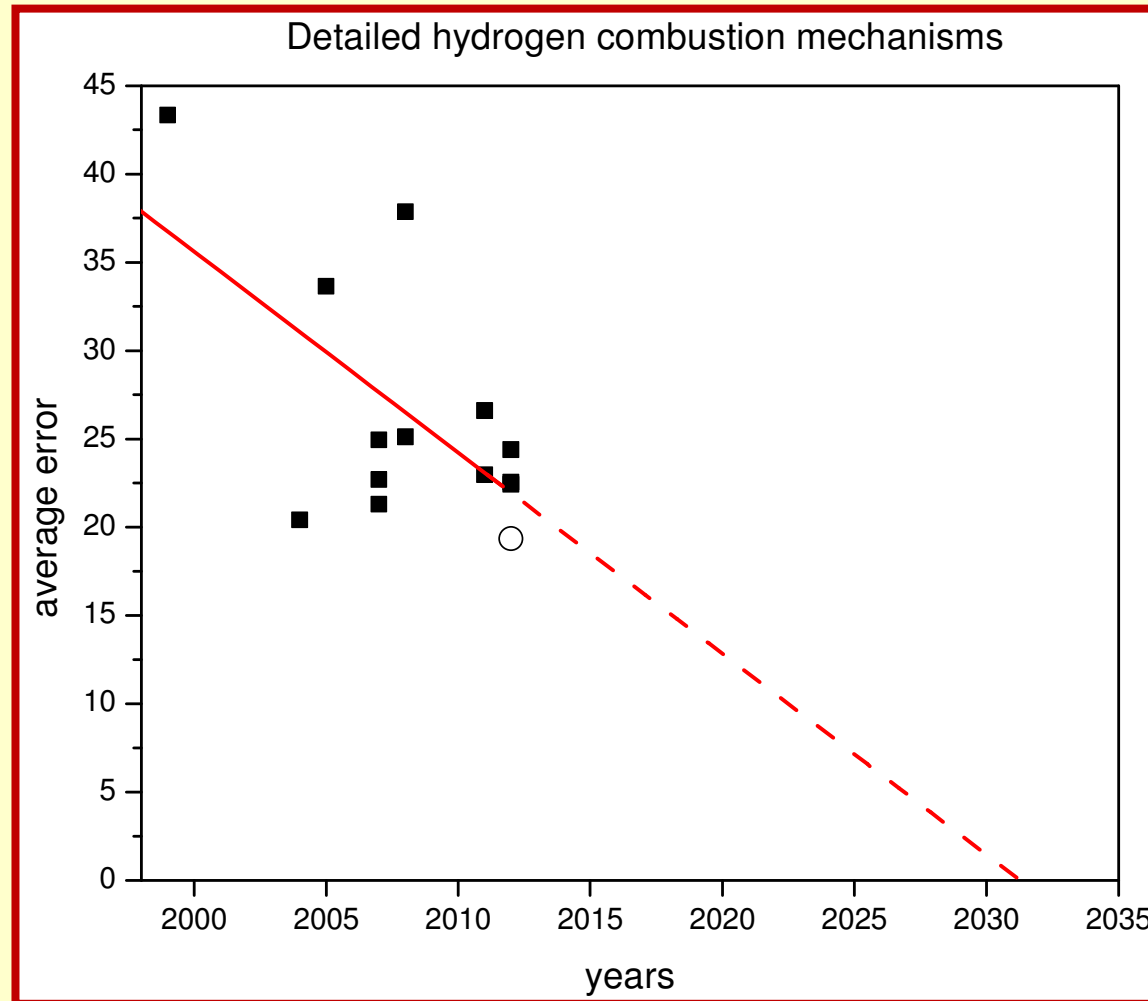


set #1: Ignition time experiments *used at the optimization*

set #2: All available ignition time experiments

set #3: All types of data (ignition time, PSR, laminar flame velocity)

The future



Based on the current trend,

the absolutely accurate hydrogen combustion mechanism

will be available on **7th March, 2032** 😊

Summary

- 1 The $f(T)$ uncertainty parameters available from the data collections are realistic, but have several shortcomings, like it refers to the uncertainty of k only.
Needed: a joint uncertainty of the rate parameters.
- 2 Assessment of the **joint uncertainty domain of the Arrhenius parameters** of a selected reaction step based on **all direct measurements and TST calculations.**
 - upper estimation of the uncertainty
 - no information about the correlation of two k values
- 3 **Comprehensive evaluation of the uncertainty of all rate parameters:**
For a given chemical kinetic system,
all direct, indirect and theoretical results are collected
assessment of the uncertainty of input data
⇒ new, physically meaningful rate parameters
⇒ information about the joint uncertainty of rate parameters

⇒ better simulation results
⇒ quantification of the uncertainty of the simulation results

Acknowledgement

For the helpful discussions

Mike J. Pilling, Judit Zádor, János Tóth

Financial support

ERA Chemistry (NN100523)

TÁMOP 4.2.1/B-09/1/KMR-2010-0003

COST CM0901 Detailed Chemical Models for Cleaner Combustion

OTKA T68256, OTKA K84054

*Thank you all
for your attention!*