Validation of detailed combustion mechanisms

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Training School on the Analysis, uncertainty quantification, validation, optimization, and reduction of combustion kinetic mechanisms

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1. Introduction: What is mechanism validation?
2. Types of indirect experimental data used for mechanism validation
3. Frequently applied methods of mechanism validation
4. Quantitative mechanism validation using a squared error function
5. Quantitative mechanism validation using curve matching (very briefly)

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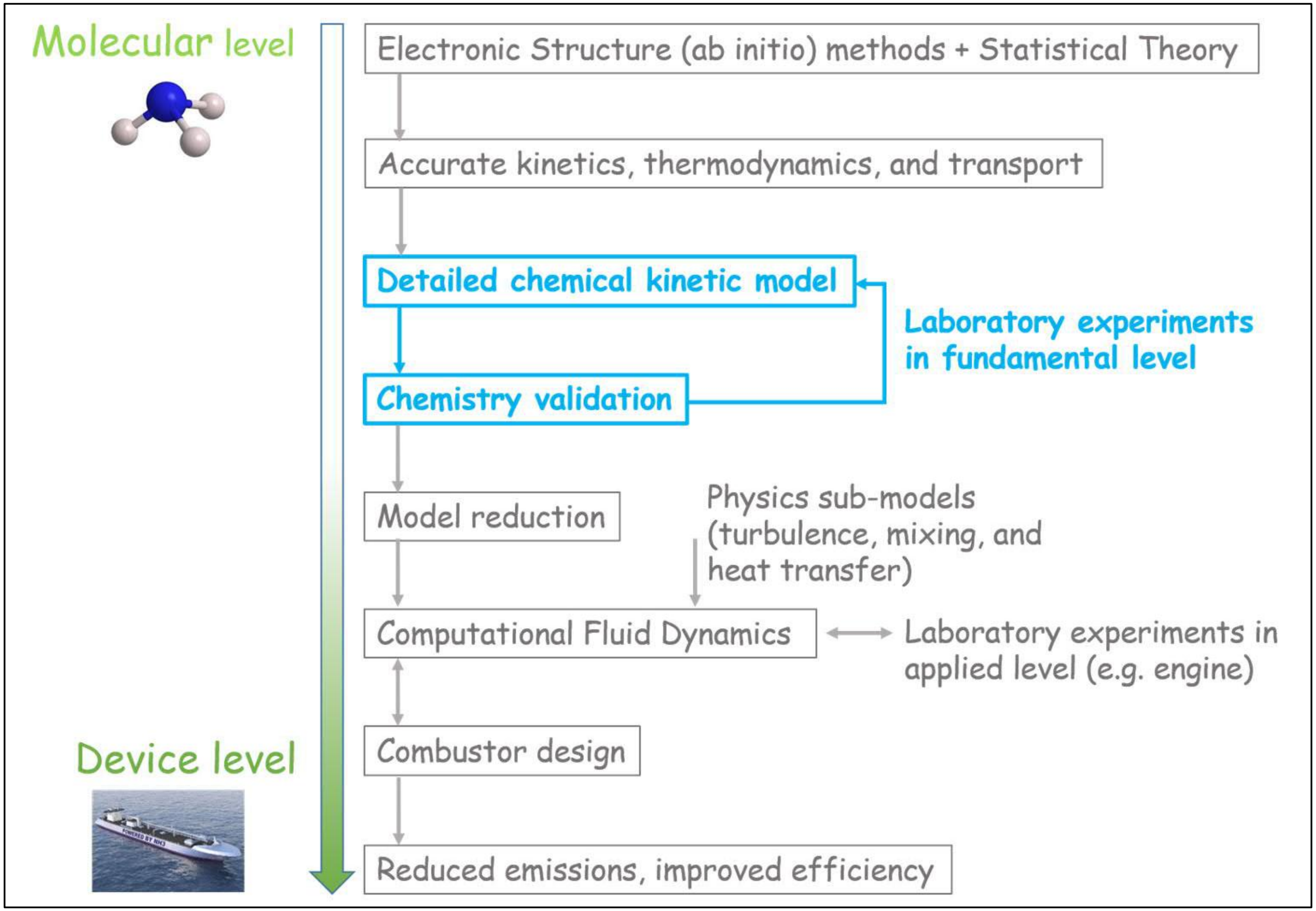
Development of combustion devices



J. Chen, PhD Thesis, Lund University (2025), redrawn from H. J. Curran, Proc. Combust. Inst. 37 (2019) 57–81.

Validation or testing?

We refer to mechanism validation as the **comparison of experimental data with the corresponding simulation results obtained using the mechanism**.

→ If the predictions of the mechanism are close to the experimental results, or at least better than the best previously published mechanism, we accept the new model.

BUT: **It does not necessarily mean that the parameters of the model are accurate** (compensation effects).

Therefore, **“testing” is a better term,**
but “validation” is used much more frequently.

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Direct and indirect experiments

- **Direct measurement**:
  - Determination of the **rate coefficient of a single reaction step** at a given temperature, pressure, and bath gas
  - Separate **experimental measurement or theoretical calculation** for each elementary reaction step
  - Typically used for **assembling** a detailed kinetic mechanism

- **Indirect measurement**:
  - Measurement of a **quantity characteristic of the whole combustion process** (concentrations, IDTs, LBVs)
  - Can be interpreted only with a simulation using a detailed combustion kinetic mechanism
  - Typically used for **validating** a detailed kinetic mechanism

Indirect experiments

- We would like to validate the **chemistry** of the detailed mechanism (rate parameters, maybe thermochemical data)
- Detailed combustion kinetic mechanisms may be very large (1,000's of species, 10,000's of reactions)

⬇

Indirect experiments **simplify complicated physical problems** (mixing, flow, heat transfer, etc.) taking place in real devices.

- **Homogeneous** (0D) **"kinetic" reactors, laminar flames** (1D)
- **Each method has limited operating *T* and *p* ranges**
  → they need to be combined to validate chemical kinetic mechanisms over a wide range of conditions

Types of indirect experiments

Homogeneous reactors (0D)

- **Ignition delay time measurements (IDT)**

Shock Tube (**ST**)

Rapid Compression Machine (**RCM**)

- **Concentration measurements**

Tubular Flow Reactor (**TFR/FR**)

Jet-Stirred Reactor (**JSR**)

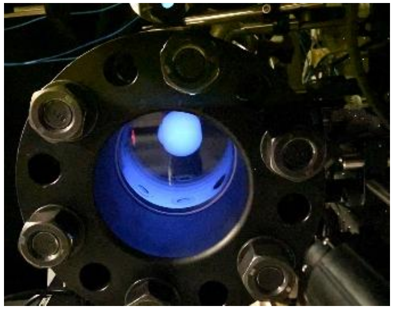
Shock Tube (**ST**)

Types of indirect experiments

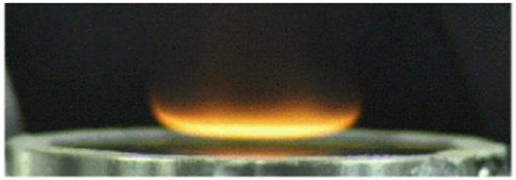
Premixed laminar flames (1D)

- **Laminar burning velocity measurements (LBV)** – several methods

Flame Cone Method

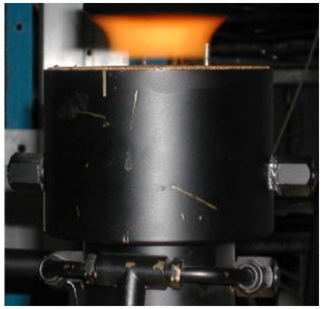


Spherical Bomb



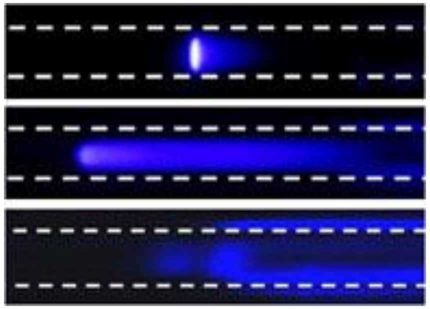
Heat Flux Burner

- **Concentration measurements**



Burner Stabilized Flame (**BSF**)

Burner Stabilized Stagnation Flame (**BSSF**)

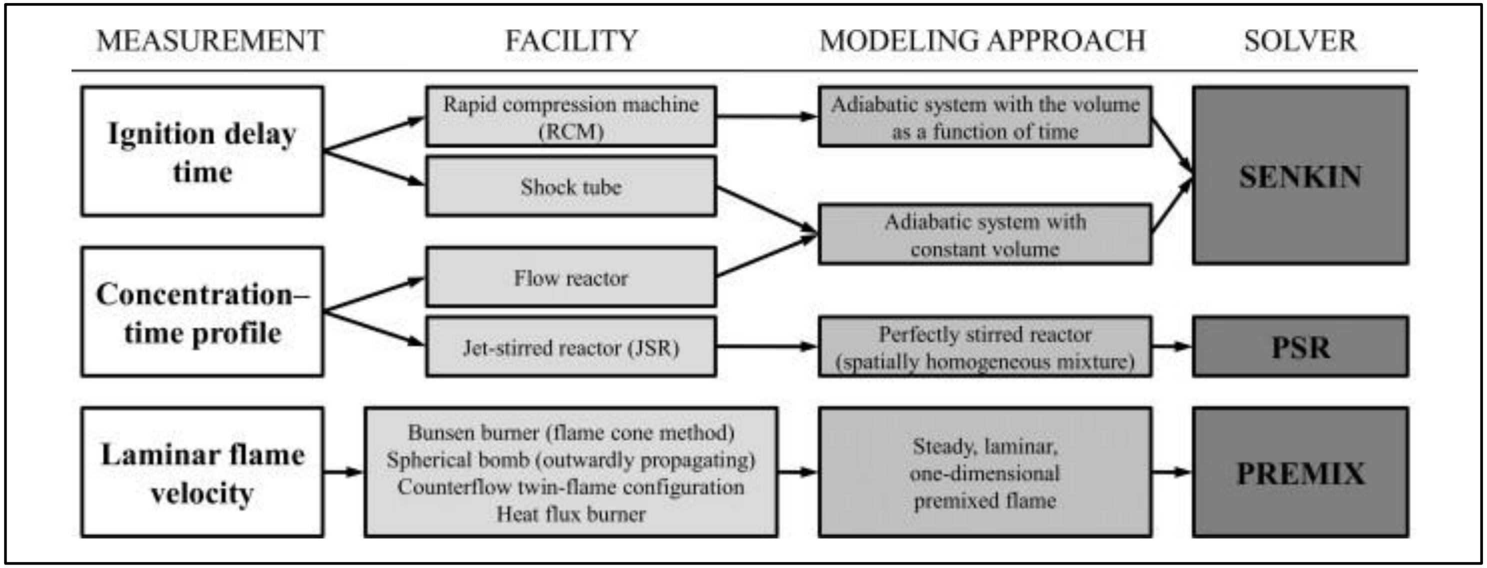


Micro Flow Reactor (**MFR**)

Simulation of indirect experiments

- Several **combustion simulation programs** are available (e.g., CHEMKIN-II, Cantera, OpenSMOKE++, FlameMaster)

- **0D simulations**: kinetic + thermochemical data
  1D simulations: kinetic + thermochemical + transport data



CHEMKIN-II simulation codes [C. Olm et al., Combust. Flame 161 (2014) 2219–2234.]

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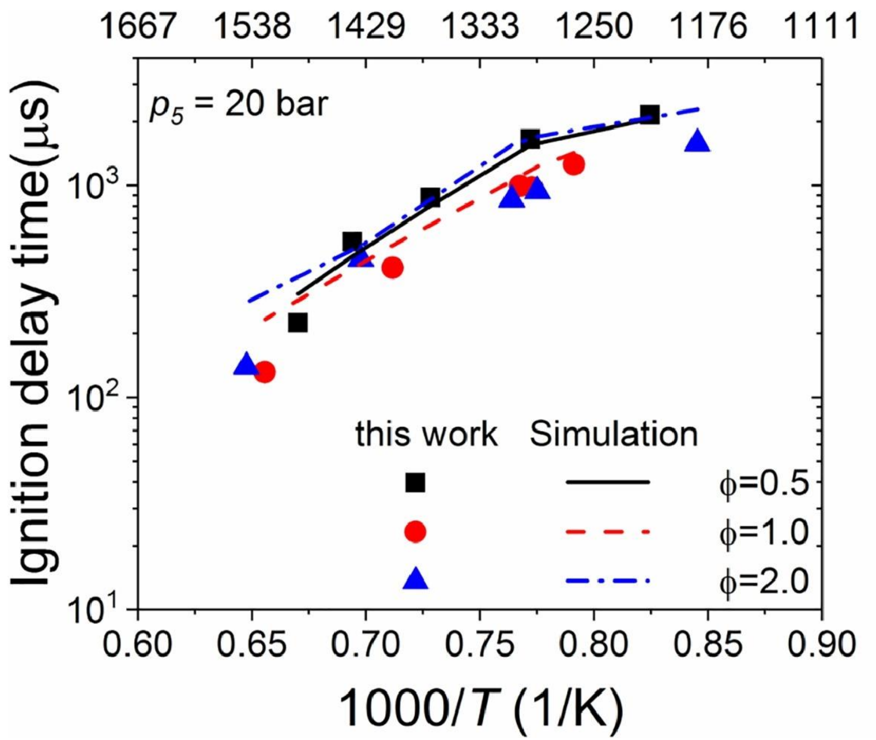
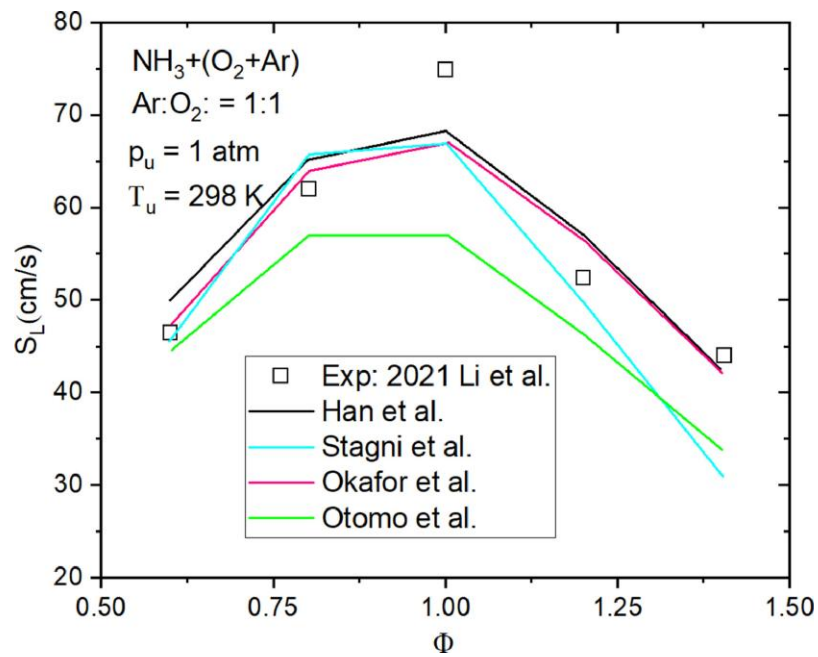
“Visual” mechanism validation

Most widely used mechanism validation method



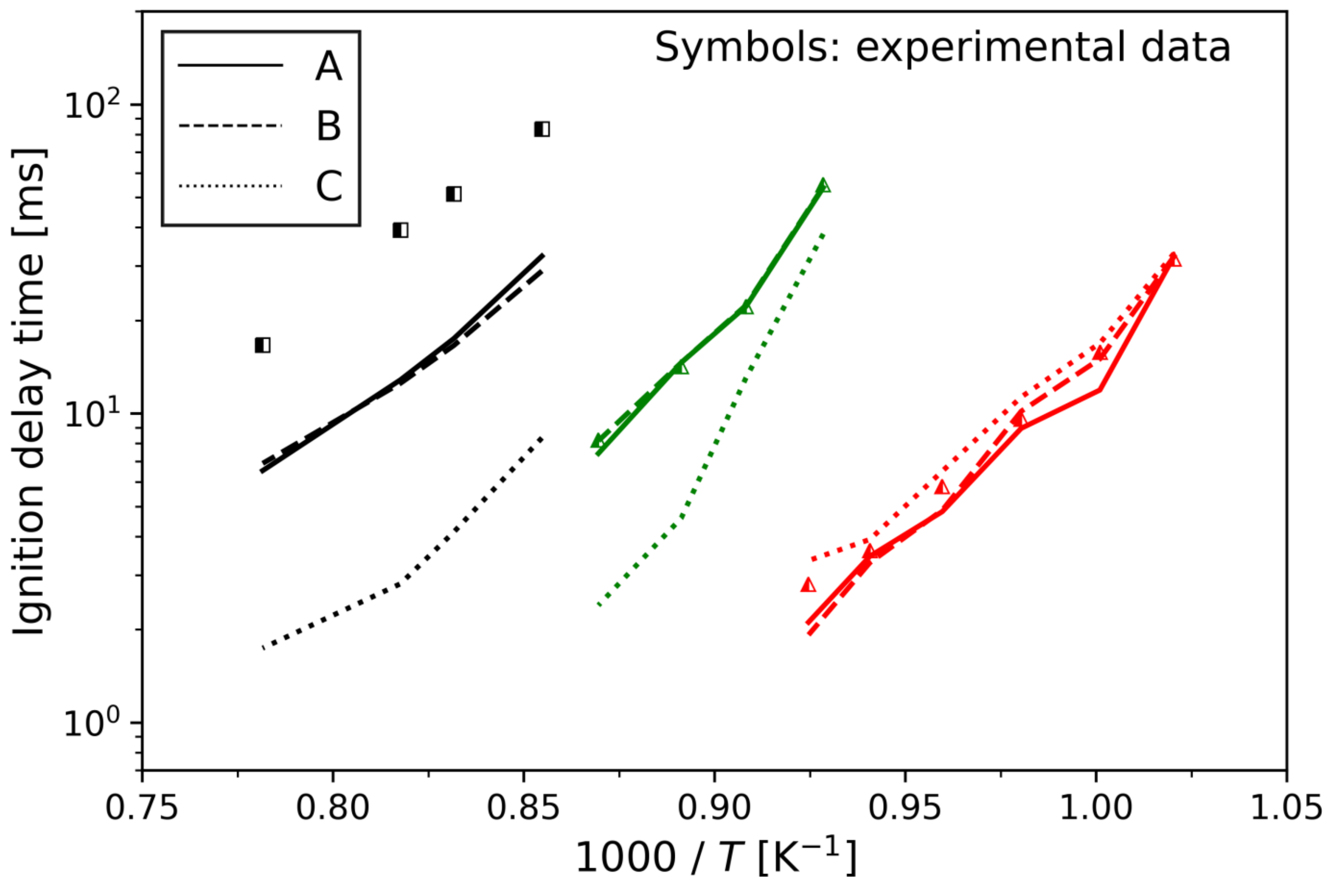


B. Shu et al., *Proc. Combust. Inst*. 37 (2019) 205–211. J. Chen et al., *Combust. Flame* 255 (2023) 112930.

Typically, **5–10 such figures in the paper**, many more in the SM

"Visual" mechanism validation – issues

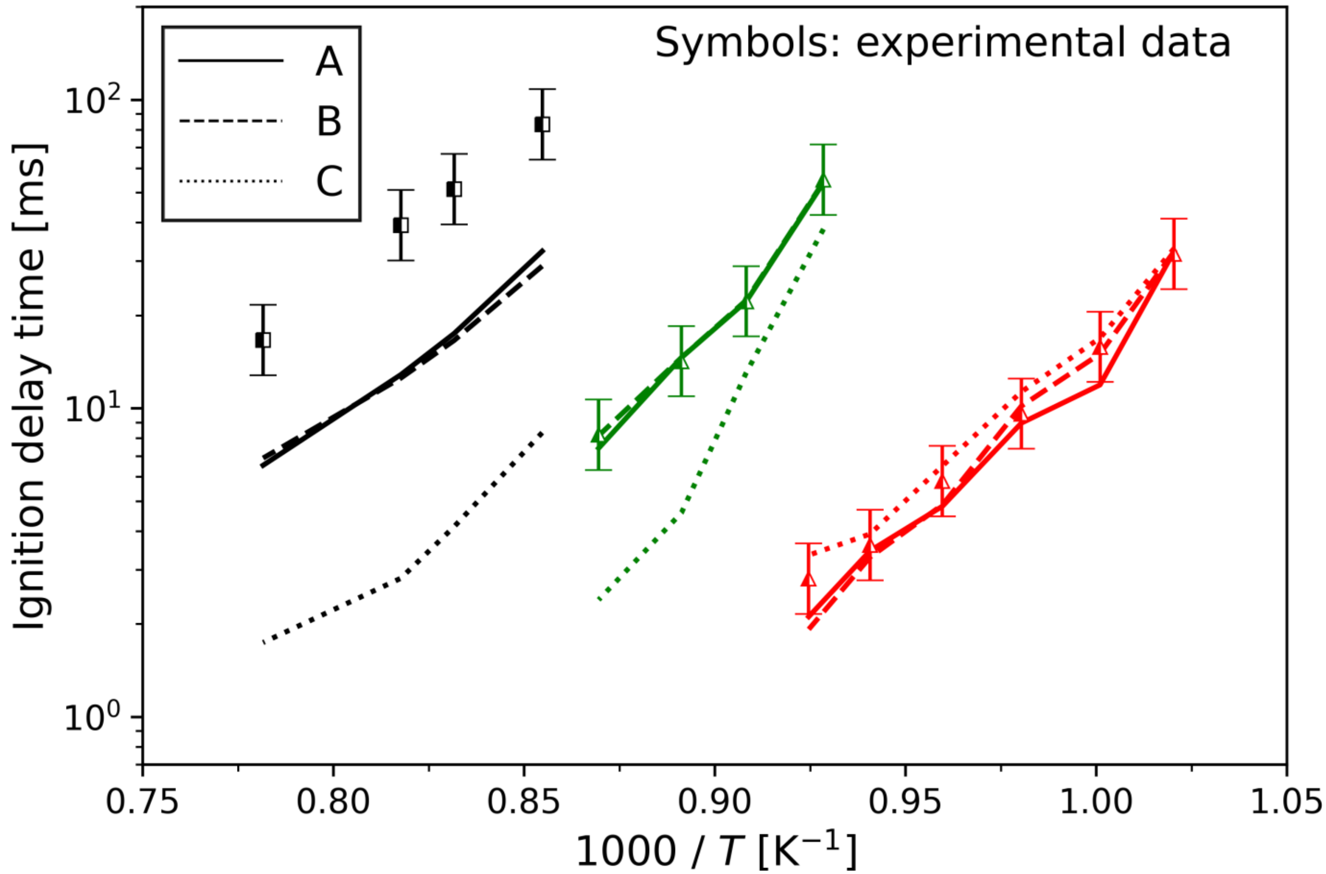
Uncertainty of the experimental data?



Exp. data: W. Liao et al., *Proc. Combust. Inst*. 39 (2023) 4377–4385.,
L. Dai et al., *Combust. Flame* 215 (2020) 134–144.

“Visual” mechanism validation – issues

Uncertainty of the experimental data?



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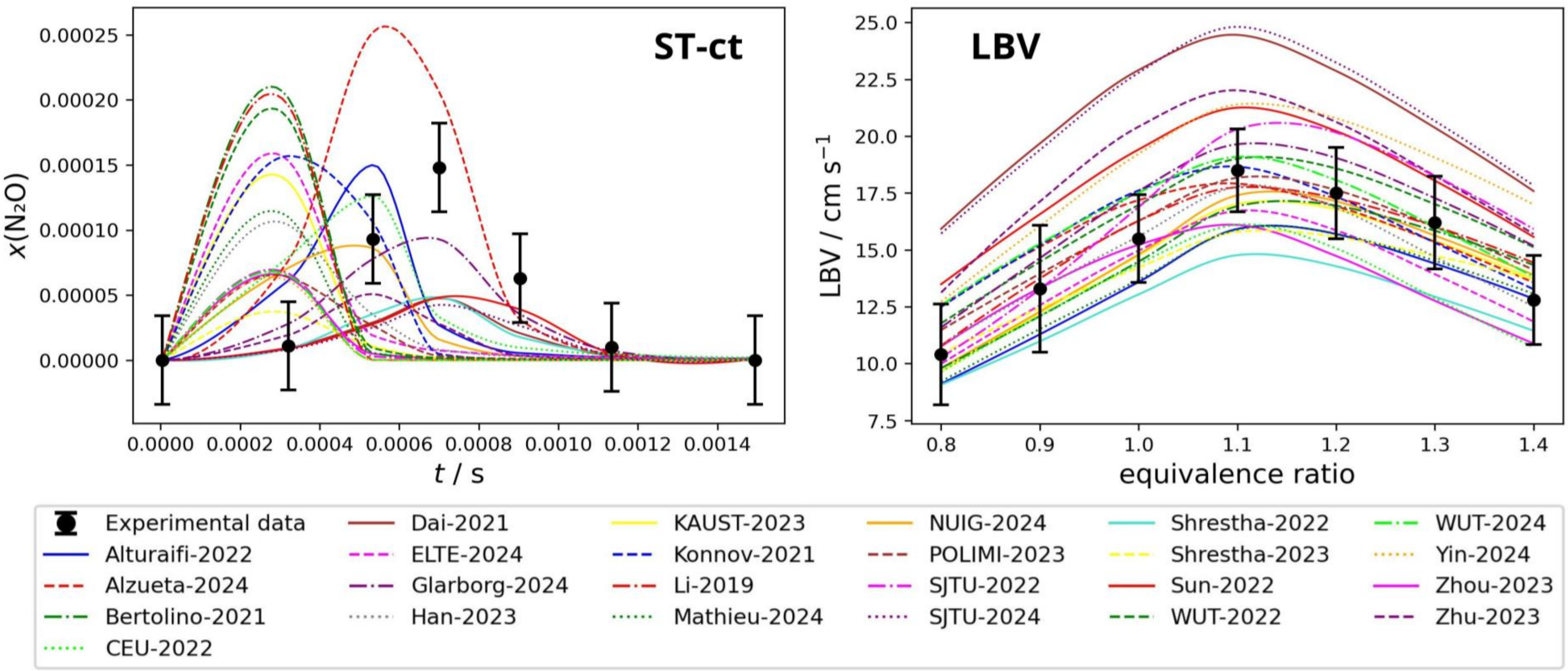
"Visual" mechanism validation – issues



100–1000's of data series and many (20+) mechanisms:
Impossible to decide which mechanism is the best overall
→ **A quantitative method is necessary!**

Quantitative mechanism validation
MAE and RMSE

- **Mean Absolute Error** (MAE)

$$MAE = \frac{1}{n}\sum_{i=1}^{n}\left|Y_i^{\mathrm{exp}} - Y_i^{\mathrm{sim}}\right|$$

n: number of data points
Y_i^{exp}: i-th experimental result
Y_i^{sim}: i-th simulation result

- **Root-Mean-Square-Error** (RMSE)

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(Y_i^{\mathrm{exp}} - Y_i^{\mathrm{sim}}\right)^2}$$

Issues:

- Not dimensionless → different measurement types cannot be compared
- Experimental uncertainties are not considered

Quantitative mechanism validation

MAPE

- **Mean Absolute Percentage Error** (MAPE)

$$MAPE = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{Y_i^{\mathrm{exp}} - Y_i^{\mathrm{sim}}}{\boldsymbol{Y_i^{\mathrm{exp}}}}\right|$$

Advantage:

- Dimensionless

Issues:

- Experimental uncertainties are not considered
- Failes for $Y_i^{\mathrm{exp}} = 0$
- Failes for very small Y_i^{exp} values → errors will be exaggerated, especially problematic for concentration measurements

Quantitative mechanism validation
MAPE using many-model-average

- **MAPE using many-model-average** (MAPE')

$$MAPE' = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{Y_i^{\mathrm{exp}} - Y_i^{\mathrm{sim}}}{\overline{\boldsymbol{Y}_i^{\mathbf{sim}}}}\right|$$

$\overline{\boldsymbol{Y}_i^{\mathbf{sim}}}$: averaged i-th simulation result for many (arbitrarily selected) models

Advantage:

- Dimensionless

Issues:

- Experimental uncertainties are not considered
- Performance of one mechanism depends on that of the others → Involving more and more very bad mechanisms will artificially improve the performance of other mechanisms

Quantitative mechanism validation

Experimental-uncertainty-normalized RMSE

- **Experimental-uncertainty-normalized Root-Mean-Square-Error** (RMSE)

$$\widetilde{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{Y_i^{\mathrm{exp}} - Y_i^{\mathrm{sim}}}{\boldsymbol{\sigma}\left(\boldsymbol{Y_i^{\mathrm{exp}}}\right)}\right)^2}$$

$\boldsymbol{\sigma}\left(\boldsymbol{Y_i^{\mathrm{exp}}}\right)$: standard deviation of the i-th experimental data point

Root-mean-square deviation of the simulation results from the experimental data relative to the experimental uncertainties, which **measures within how many σ experimental standard deviations the model can reproduce the experimental results**, on average.

$\widetilde{RMSE} = 1 \rightarrow 1\sigma$

$\widetilde{RMSE} = 2 \rightarrow 2\sigma$, etc.

Quantitative mechanism validation

Experimental-uncertainty-normalized RMSE

Why summing the squared and not the absolute deviations?

Assuming the Y_i^{exp} data are

- independent and
- follow normal distribution,

$Z_i = \frac{Y_i^{\mathrm{exp}} - Y_i^{\mathrm{sim}}}{\sigma(Y_i^{\mathrm{exp}})}$ is a standard normal random variable. Then,

$$\widetilde{RMSE}^2 = \frac{1}{n}\sum_{i=1}^{n} Z_i^2 \sim \chi_1^2 \qquad \text{(assuming } n \text{ is large)}$$

Hence, we can make use of the properties and statistical inference of the **reduced chi-square distribution**.

Quantitative mechanism validation
Experimental-uncertainty-normalized RMSE

A value of $\widetilde{RMSE} = 1$ indicates that the average deviation between the experimental data and the simulation results matches the uncertainty of the experimental data (σ).

- **A model with $\widetilde{RMSE} = 1$ can be considered "perfect"**, i.e., it captures all features of the data except the noise
- **Real combustion kinetic models have $\widetilde{RMSE} > 1$** for large collections of experimental data (**underfitting**), and **the smaller the $\widetilde{RMSE}$ value, the better the model**
- $\widetilde{RMSE} < 1$ indicates **overfitting** – it **never occurs for real combustion kinetic models for sufficiently large n-s**

Quantitative mechanism validation

Experimental-uncertainty-normalized RMSE

The **absolute values** $|Z_i|$ do *not* follow normal distribution, and there is *no* analoguous χ distribution for their sum

$$\frac{1}{n}\sum_{i=1}^{n}|Z_i|$$

Hence, ***no* statistical inference could be attributed to the resulting quantity**.

Quantitative mechanism validation
Experimental-uncertainty-normalized RMSE

Squared deviations correspond to Euclidean (L^2) distance in high-dimensional space. If **the $\widetilde{RMSE}^2$ function is used as a target function in model fitting**, **it corresponds to least squares parameter optimization**.
Hence, we can make use of the favorable properties of least squares fitting, assuming normally distributed data:
The estimations of the parameters will be unbiased and have minimum variance.

Absolute values lead to Manhattan (L^1) distance in high-dimensional space. Hence, **we cannot make use of favorable properties of least squares fitting**.

Quantitative mechanism validation
Experimental-uncertainty-normalized RMSE

Advantages of $\widetilde{RMSE}$:

- Dimensionless
- Experimental uncertainties are considered
- Statistical inference can be attributed to its value
- Can easily be used in least squares parameter optimization

The application of the $\widetilde{RMSE}$ measure
to combustion kinetic mechanism validation
will be discussed in the next section of the lecture.

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The error function *E*

Indirect experimental data are arranged in data series.

Data point: A single observation, e.g.,
LBV measured at a given T, p, and gas mixture composition.

Data series: One quantity measured sequentially as a function of an independent, systematically changed quantity, e.g.,
LBVs measured at different T-s
at a given p and gas mixture composition.

Data collection: Several data series.

The error function *E*

Let the experimental data collection consist of *N* data series, and let each data series *s* contain N_s data points.

$$E_{sd} = \left(\frac{Y_{sd}^{\exp} - Y_{sd}^{\mathrm{sim}}}{\sigma\left(Y_{sd}^{\exp}\right)} \right)^2$$

for the *d*-th **data point** in the *s*-th data series

$$E_s = \frac{1}{N_s} \sum_{d=1}^{N_s} E_{sd}$$

for the *s*-th **data series**

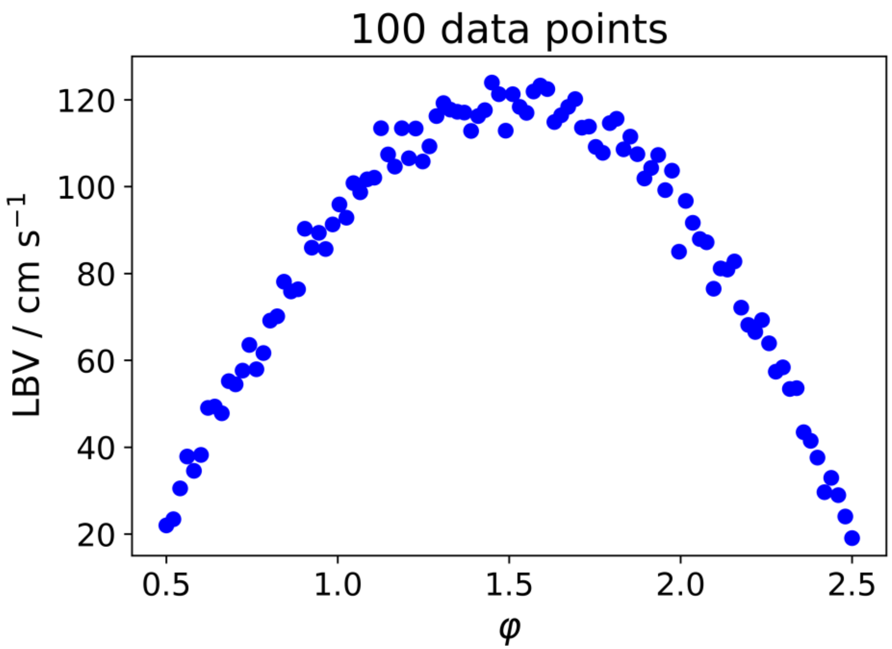
$$E = \frac{1}{N} \sum_{s=1}^{N} E_s$$

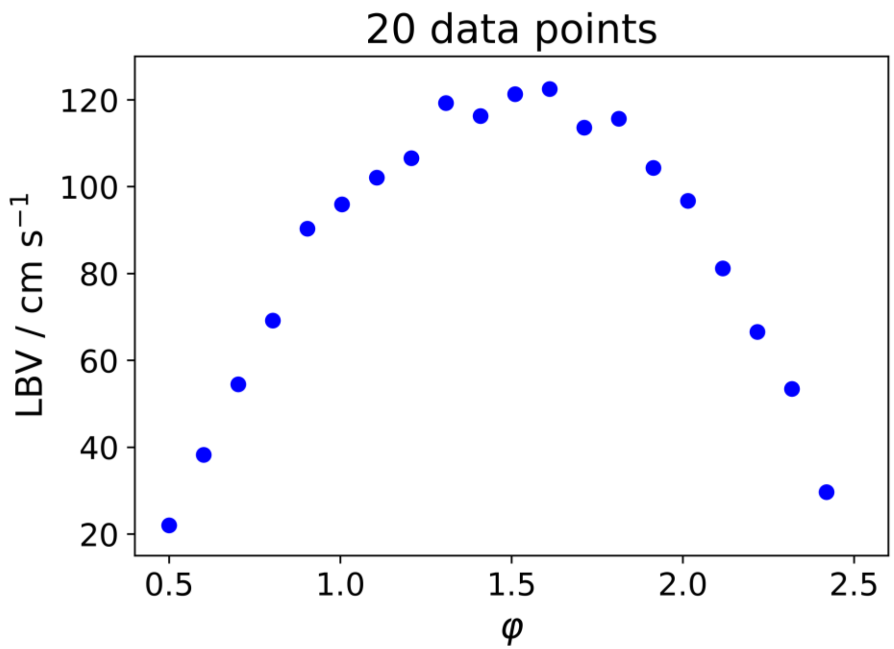
for the whole **data collection**

The error function *E*

$$E = \frac{1}{N}\sum_{s=1}^{N}\frac{\mathbf{1}}{\boldsymbol{N_s}}\sum_{d=1}^{N_s}\left(\frac{Y_{sd}^{\mathrm{exp}} - Y_{sd}^{\mathrm{sim}}}{\sigma\left(Y_{sd}^{\mathrm{exp}}\right)}\right)^2$$

Each data series has equal weight in *E*





The error function *E*

$$E = \frac{1}{N}\sum_{s=1}^{N}\frac{1}{N_s}\sum_{d=1}^{N_s}\left(\frac{Y_{sd}^{\exp} - Y_{sd}^{\mathrm{sim}}}{\sigma\left(Y_{sd}^{\exp}\right)}\right)^2$$

$\sqrt{E}$ is the root-mean-square deviation of the simulation results from the experimental data relative to the experimental uncertainties, which **measures within how many σ experimental standard deviations the model can reproduce the experimental results**, on average.

$\sqrt{E} = 1 \rightarrow 1\sigma$ ("perfect" model – ideal)

$\sqrt{E} = 2 \rightarrow 2\sigma$ (excellent model in practice)

$\sqrt{E} = 3 \rightarrow 3\sigma$ (good model in practice)

The error function *E*

$$E = \frac{1}{N}\sum_{s=1}^{N}\frac{1}{N_s}\sum_{d=1}^{N_s}\left(\frac{Y_{sd}^{\mathbf{exp}} - Y_{sd}^{\mathbf{sim}}}{\sigma\left(Y_{sd}^{\mathbf{exp}}\right)}\right)^2$$

$$Y_{sd}^{\mathbf{exp/sim}} = \begin{cases} y_{sd}^{\mathbf{exp/sim}} & \text{if } y_{sd}^{\mathbf{exp}} \text{ has normal distribution} \\ \ln y_{sd}^{\mathbf{exp/sim}} & \text{if } y_{sd}^{\mathbf{exp}} \text{ has lognormal distribution} \end{cases}$$

- $y_{sd}^{\mathbf{exp/sim}}$: untransformed measured/simulated result

LBV, concentration: normal distribution is assumed
→ **absolute errors**: $\sigma\left(y_{sd}^{\mathrm{exp}}\right)$

IDT data: lognormal distribution is assumed
→ **relative errors**: $\approx \sigma\left(\ln y_{sd}^{\mathrm{exp}}\right)$ for small errors (e.g., <20%)

Experimental uncertainties – issues

The main problem is the proper estimation of the uncertainty of the experimental data (σ)

Typical cases:

- Uncertainties are not published with the experimental data (very rare in recently published papers)
- The given uncertainty is too optimistic and not realistic
- The published uncertainty assessment considers only a few sources of possible errors
- Uncertainty assessment is very comprehensive and of good quality (can sometimes be found in recently published papers)

Experimental uncertainties – solution

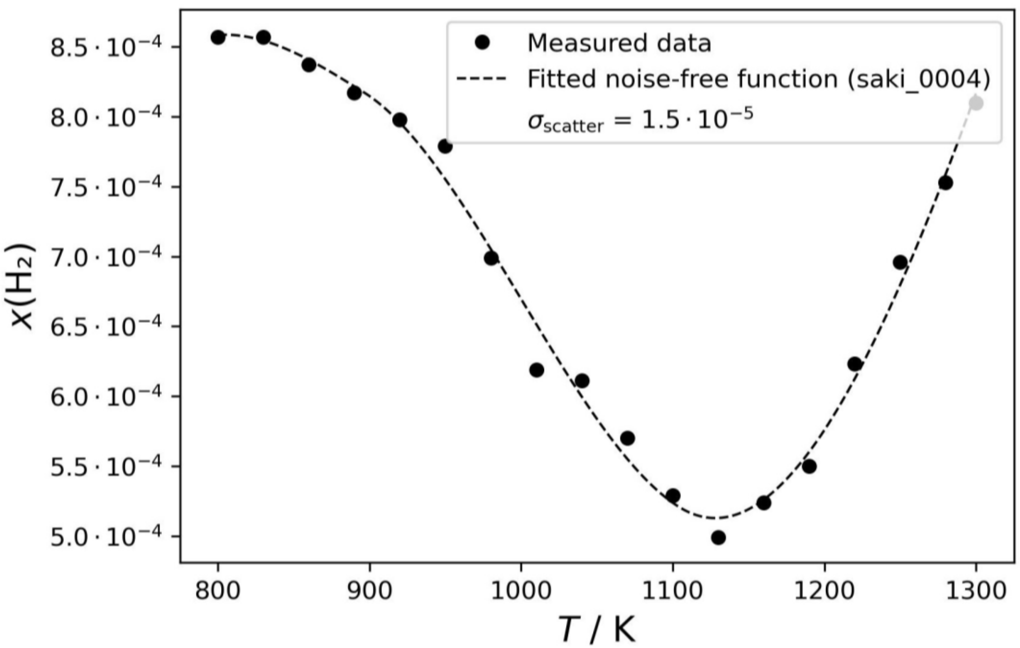
In most of our previous publications, two uncertainty sources were considered:

$$\sigma_{sd} = \sqrt{\sigma_{sd,\mathrm{exp}}^2 + \sigma_{s,\mathrm{scatter}}^2}$$

- $\sigma_{sd,\mathrm{exp}}$: **experimental standard deviation** as published in the paper (if missing, it is assigned based on other papers using similar equipment)
- $\sigma_{s,\mathrm{scatter}}$: **estimated statistical scatter of the *s*-th data series** stemming from the scatter of repeated measurements (usually not considered in σ_{exp})

Determination of $\sigma_{s,scatter}$

$\sigma_{s,scatter}$ is obtained by **fitting a smooth trendline to the data points of the *s*-th data series**



Exp. data: K. N. Osipova et al., *Fuel* 310 (2022) 122202.

- To find the optimal trendline and determine the scatter of the data points, **Akima spline and polynomial functions** are fitted to the data series using code **Minimal Spline Fit**
- Visual inspection of the fitted function graphs is always needed!

Theory: T. Nagy, T. Turányi, *Proceedings of the ECM – 2021*, Paper 336, 14–15 April, 2021, Naples, Italy

Code: available at https://ReSpecTh.hu

Experimental uncertainties – solution

For recent LBV and IDT data, the $\sigma_{sd,\exp}$ almost always contains the uncertainty coming from the uncertainty of the initial conditions (*T*, *p*, gas mixture composition).

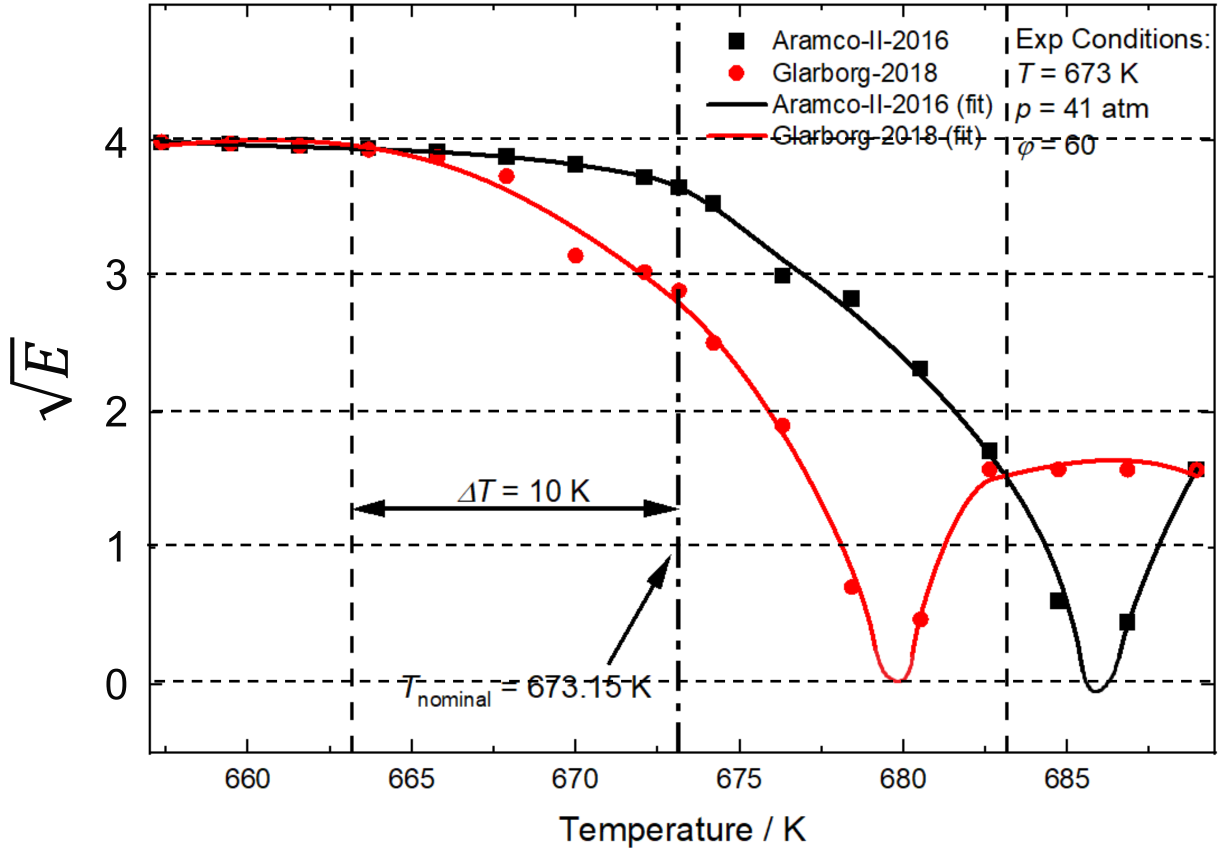
However, it is not true for **outlet concentration data**. The **uncertainty of the temperature of the measurement may induce significant uncertainty in the measured concentrations**, which is usually not considered in $\sigma_{sd,\exp}$. Therefore, another uncertainty term has to be added:

$$\sigma_{sd} = \sqrt{\sigma_{sd,\exp}^2 + \sigma_{s,\mathrm{scatter}}^2 + \boldsymbol{\sigma_{sd,\mathrm{cond}}^2}}$$

- $\boldsymbol{\sigma_{sd,\mathrm{cond}}}$: standard deviation of the measured data propagated from the uncertainty of the experimental conditions

Experimental uncertainties – solution

We showed that the **uncertainty of the measurement temperature has the largest effect** on the uncertainty of the measured outlet concentrations.

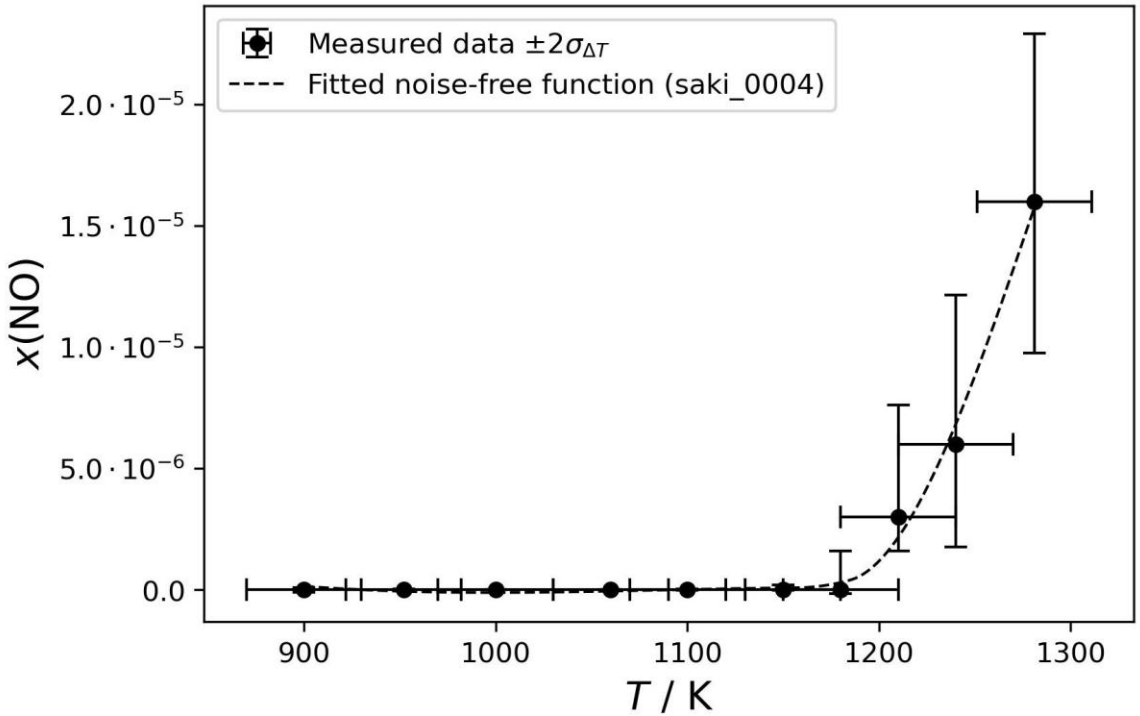


typical reaction T uncertainty: ΔT = 2–20 K

P. Zhang, I. Gy. Zsély, M. Papp, Á. Veres-Ravai, B. Su, T. Nagy, B. Yang, T. Turányi, *Combust. Flame*, under review (2025)

Experimental uncertainties – solution

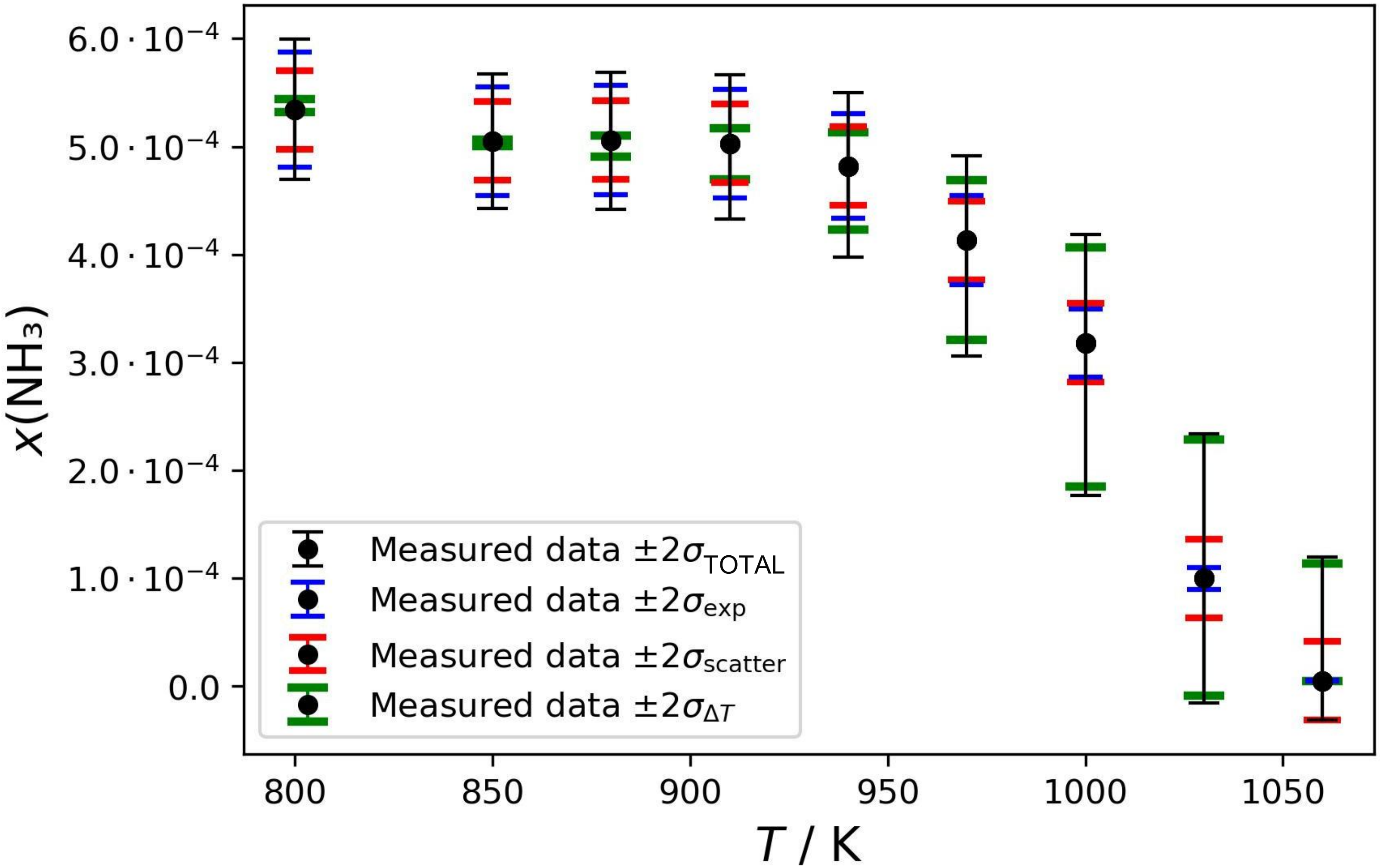
The temperature uncertainties (σ_T) were collected from the publications, and the **effect of temperature uncertainty on the uncertainty of the experimental data** ($\sigma_{\Delta T}$) **was estimated using the principle of Gaussian error propagation**.



Exp. data: X. Zhang et al., *Combust. Flame* 234 (2021) 111653.

- Uncertainty is propagated along the **noise-free trendline** obtained using Minimal Spline Fit
- The **propagated uncertainties may be asymmetric**

Experimental uncertainties – solution



Exp. data: X. Zhang et al., *Combust. Flame* 234 (2021) 111653.

Manual weighting in *E*

One may want to **emphasize one or more data series or one type of experiment**.

This can be achieved by upweighting those data series and downweighting the other ones. The **more general *E* formula**:

$$E = \frac{1}{N} \sum_{s=1}^{N} \frac{w_s}{N_s} \sum_{d=1}^{N_s} \left(\frac{Y_{sd}^{\mathrm{exp}} - Y_{sd}^{\mathrm{sim}}}{\sigma\left(Y_{sd}^{\mathrm{exp}}\right)} \right)^2$$

- w_s: weight of data series *s*

Note: $\frac{1}{N} \sum_{s=1}^{N} w_s = 1$ must apply

Example

- **NH_3 and NH_3/H_2** experimental data collection

Exp. type	N_{series}	N_{points}	T / K	p / atm	φ	H_2 % in fuel
JSR-conc	334	4917	500–1452	0.99–1.40	0.01–5.19	0–70
ST-IDT	89	624	1023–2720	1.01–41.65	0.47–2.07	0–70
LBV	445	5093	293–821	0.30–36.58	0.20–2.00	0–100
FR-conc	247	4850	451–1973	0.96–98.69	0.01–23.98	0–91
ST-ct	203	1667	1474–2720	1.15–3.59	0.50–3.46	0–49
ST-conc	9	91	1581–2720	1.15–3.59	0.50–1.84	0–21
Overall:	**1327**	**17242**	**293–2720**	**0.30–98.69**	**0.01–23.98**	**0–100**

- **32 recent NH_3 combustion mechanisms** were tested quantitatively

A. Gy. Szanthoffer, M. Papp, T. Nagy, T. Turányi, *Combust. Flame*, under review (2025)

E values

#	Mechanism	$\sqrt{E_{\text{conc}}}$	$\sqrt{E_{\text{IDT}}}$	$\sqrt{E_{\text{LBV}}}$	$\sqrt{E_{\text{overall}}}$
1	**NUIG-2024**	6.5	3.6	3.4	**4.7**
2	**UCF-2024**	6.6	3.4	4.0	**4.9**
3	**Tsinghua-2024c**	7.1	5.0	3.0	**5.3**
4	**Alturaifi-2022**	7.9	3.0	3.8	**5.4**
5	**QUST-2024**	8.1	3.1	3.7	**5.4**
6	**KAUST-2023**	7.9	4.8	3.0	**5.6**
7	**Tsinghua-2024b**	8.0	4.9	3.0	**5.7**
8	**Tsinghua-2024a**	8.6	3.7	3.2	**5.7**
9	**Zhu-2023**	7.3	3.3	5.8	**5.7**
10	**POLIMI-2023**	8.2	4.3	3.8	**5.8**
11	**Bertolino-2021**	8.9	3.9	2.9	**5.9**
12	**Glarborg-2024**	8.4	6.0	3.1	**6.2**
13	**HUST-2024**	8.3	4.7	5.3	**6.3**
14	**Mathieu-2024**	9.0	5.4	3.2	**6.3**
15	**Han-2023**	9.9	4.2	2.5	**6.4**
16	**Meng-2024**	10.1	3.7	2.9	**6.4**
17	**Wang-2023**	10.1	3.9	3.2	**6.6**
18	**Shrestha-2022**	8.3	5.2	5.7	**6.6**
19	**Sun-2022**	8.7	4.9	5.7	**6.6**
20	**Konnov-2021**	11.0	3.9	3.0	**6.9**
21	**WUT-2022**	10.5	4.5	4.3	**7.0**
22	**Kwon-2024**	9.2	5.3	6.2	**7.1**
23	**Yin-2024**	9.0	6.2	6.1	**7.2**
24	**WUT-2024**	11.0	4.6	3.7	**7.2**
25	**Dai-2021**	7.9	4.5	9.1	**7.4**
26	**Nakamura-2024**	11.0	5.0	4.7	**7.5**
27	**CEU-2022**	11.9	4.6	3.8	**7.7**
28	**SJTU-2024**	9.4	4.8	9.2	**8.1**
29	**ELTE-2024**	12.6	6.6	3.2	**8.4**
30	**Yu-2024**	13.2	3.4	5.9	**8.6**
31	**Alzueta-2024**	21.7	5.1	4.1	**13.1**
32	**Liu-2024**	17.5	31.0	15.2	**22.4**

Failed simulations

Issue:

Some data points cannot be simulated with one or more mechanisms due to numerical instability (solver issue, stiffness, etc.). This may typically occur for 1D simulations.

- We have a different number of successfully simulated data points for each mechanism
- *E* values for different numbers of data points cannot be compared

Solution:

These data points should be excluded from the comparison.

- If only a few data points (1–2%) are involved, it is OK, because we do not lose much information
- If many simulations fail with a mechanism, it is recommended to exclude that mechanism to minimize data loss

Failed simulations

32 + 4 mechanisms:

#	Mechanism	$\sqrt{E_{\mathrm{conc}}}$	$\sqrt{E_{\mathrm{IDT}}}$	$\sqrt{E_{\mathrm{LBV}}}$	$\sqrt{E_{\mathrm{overall}}}$
1	NUIG-2024	6.5	3.6	3.4	**4.7**
2	UCF-2024	6.6	3.4	4.0	**4.9**
3	Tsinghua-2024c	7.1	5.0	3.0	**5.3**
⋮					
30	Yu-2024	13.2	3.4	5.9	**8.6**
31	Alzueta-2024	21.7	5.1	4.1	**13.1**
32	Liu-2024	17.5	31.0	15.2	**22.4**
	HUST-2023	10.5	4.1	–	**–**
	Li-2019	12.9	3.8	–	**–**
	SJTU-2022	9.8	6.1	–	**–**
	Zhou-2023	11.7	7.8	–	**–**

Usually, it turns out that these mechanisms are also not the best for the other types of experiments.

Inconsistent experimental data

Issue:

Mechanism validation must be based on reliable, consistent data.

- The experimental data should not have systematic errors
- Their uncertainty should be realistic

Even though we are cautious with the selection and uncertainty estimation of the experimental data, we cannot be sure.

Solution 1:

Those data points are excluded that none of the mechanisms can reproduce within their 3σ (or 4σ, 5σ etc.) uncertainty limits.
Usually, about 5% of the data are excluded based on this criterion.

Problem with this approach:
Some experimental conditions (p, T, φ) may not be well described by any of the mechanisms → good data points may be excluded!

Inconsistent experimental data

Solution 2:

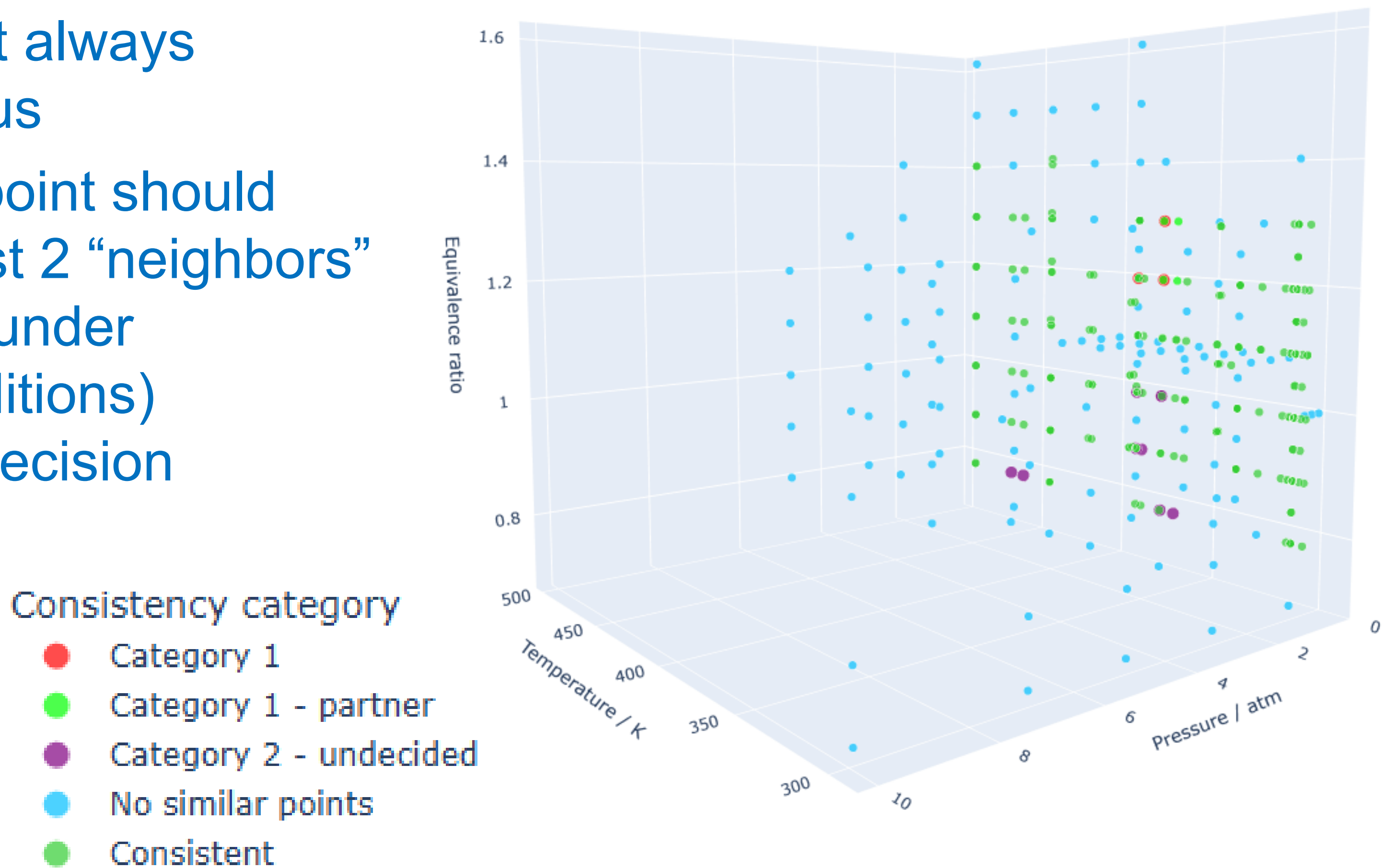
- A given type of experiment is selected (e.g., NH_3/air LBV)
- Bins are defined around each data point in the space of the relevant condition variables (e.g., T, p, φ). The edges of the bins correspond to ΔT, Δp, $\Delta\varphi$, etc.
- Experimental data belonging to the same bins (measured under similar conditions) are compared. If their uncertainty intervals do not overlap, they are labeled as inconsistent and excluded.

A. Gy. Szanthoffer, M. Papp, T. Turányi,
Identification of well-parameterised reaction steps in detailed combustion mechanisms – a case study of ammonia/air flames,
Fuel 380 (2025) 132938.

Inconsistent experimental data

Problems with this approach:

- Determination of the bin edges is not always unambiguous
- Each data point should have at least 2 “neighbors” (measured under similar conditions) to make a decision



Inconsistent experimental data

Solution 3:

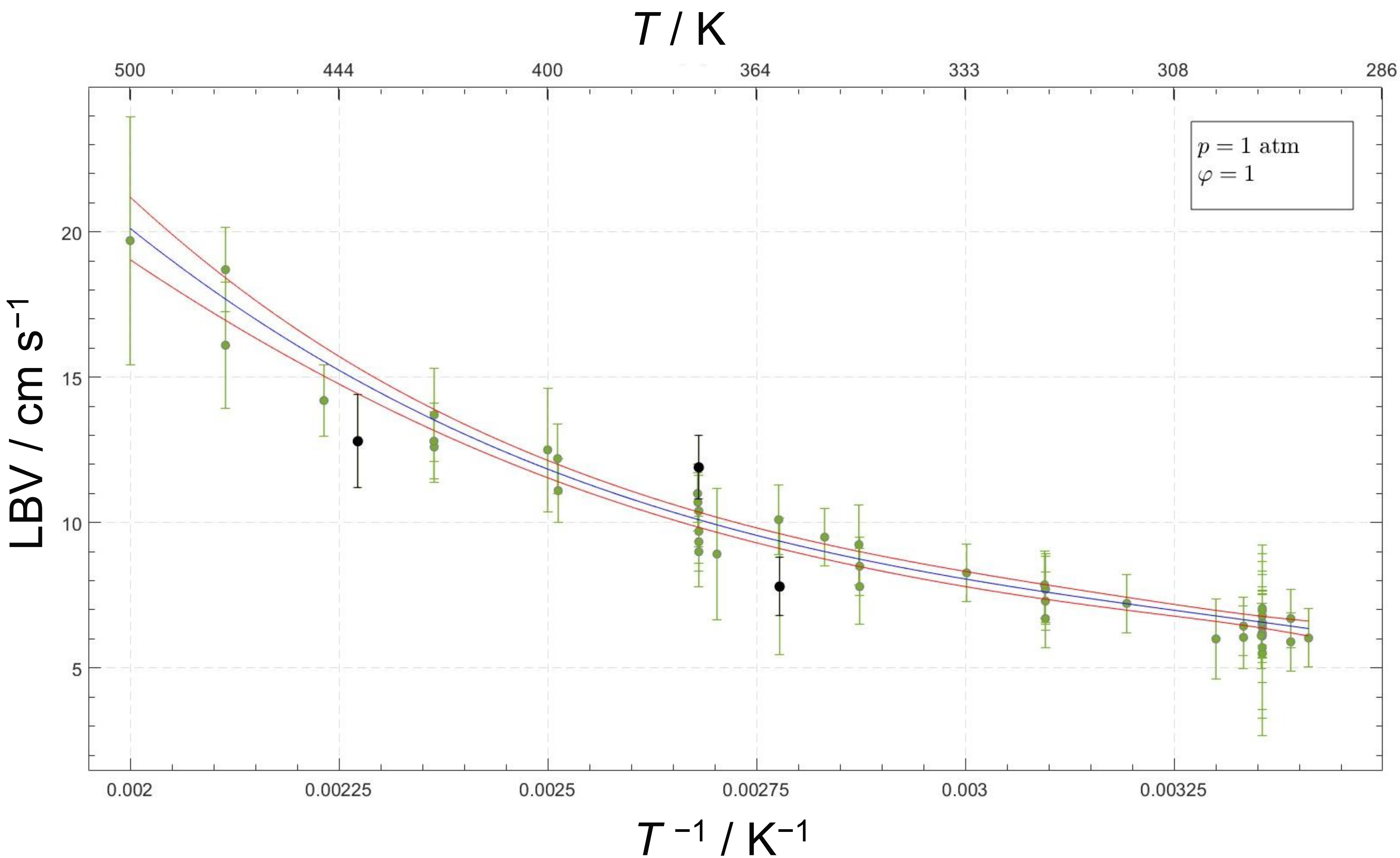
- A given type of experiment is selected (e.g., NH_3/air LBV)
- The data are fitted by a polynomial in the space of the relevant condition variables (e.g., p, T, φ)
- Experimental data points that are far from the fitted polynomial surface are labeled as outliers and excluded

É. Valkó, T. Nagy et al., *manuscript in preparation*

Possible problems with this approach:

- Polynomials may be good for fitting LBV and IDT data, but they will probably not be good for concentration data
- If we need to consider too many variables, the amount of data available may not be enough for a good fit

Inconsistent experimental data



Stacked bar plots

Issue:

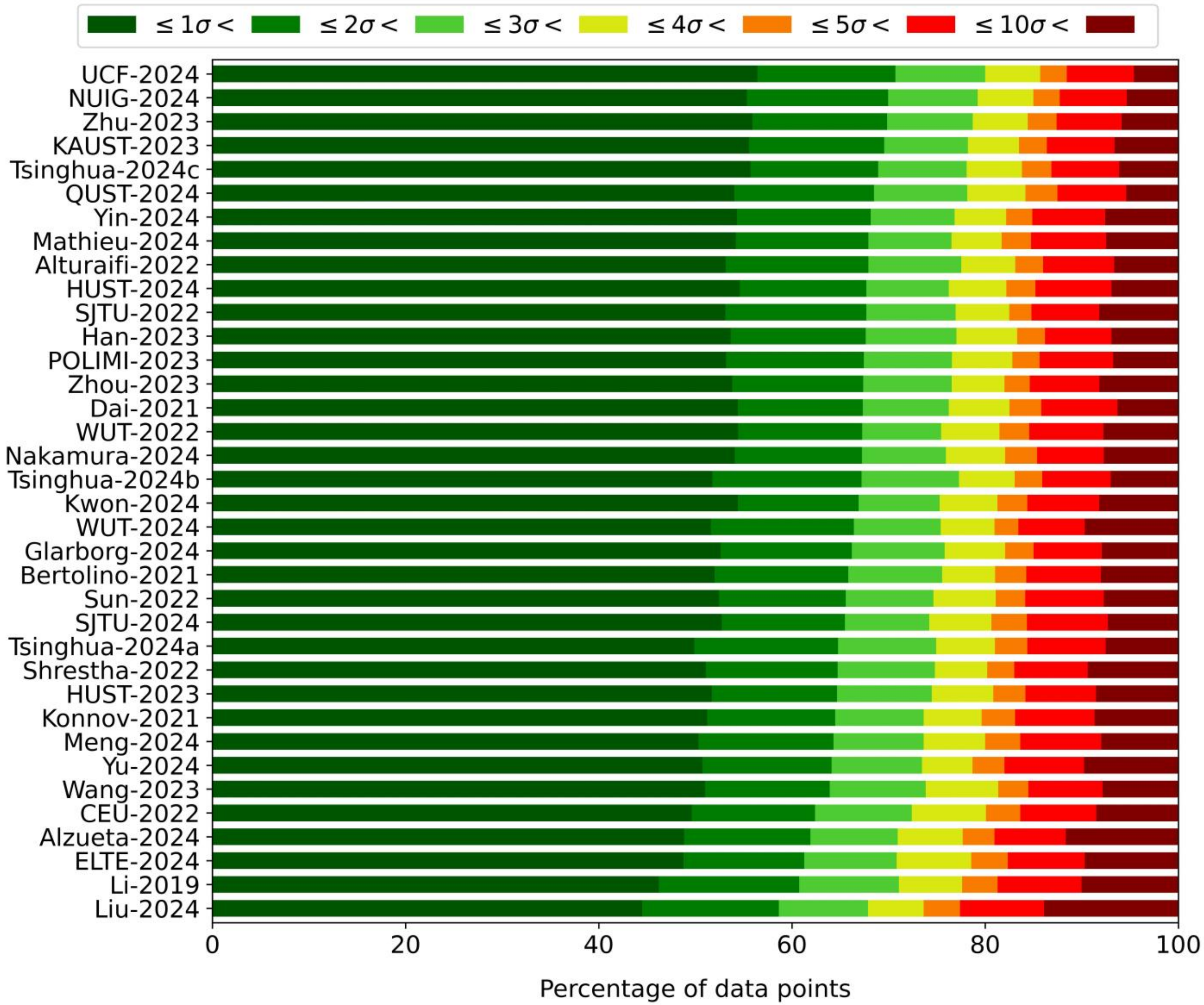
The $\sqrt{E_{sd}}$ value may be extremely high (i.e., 100's or 1000's) with one or more (but not all!) of the mechanisms for a few data points if the simulation result differs from the experimentally measured value by order(s) of magnitude.
These few data points ("outliers") can significantly increase the overall $\sqrt{E}$ value of the corresponding mechanism, which would lead us to false impressions about the overall performance of the mechanism.

Solution:

We can investigate the distribution of the $\sqrt{E_{sd}}$ values instead of the root-mean-square of the E_{sd} values ($\sqrt{E}$) if there many data points with extremely high $\sqrt{E_{sd}}$ values
→ visualization: **stacked bar plots**

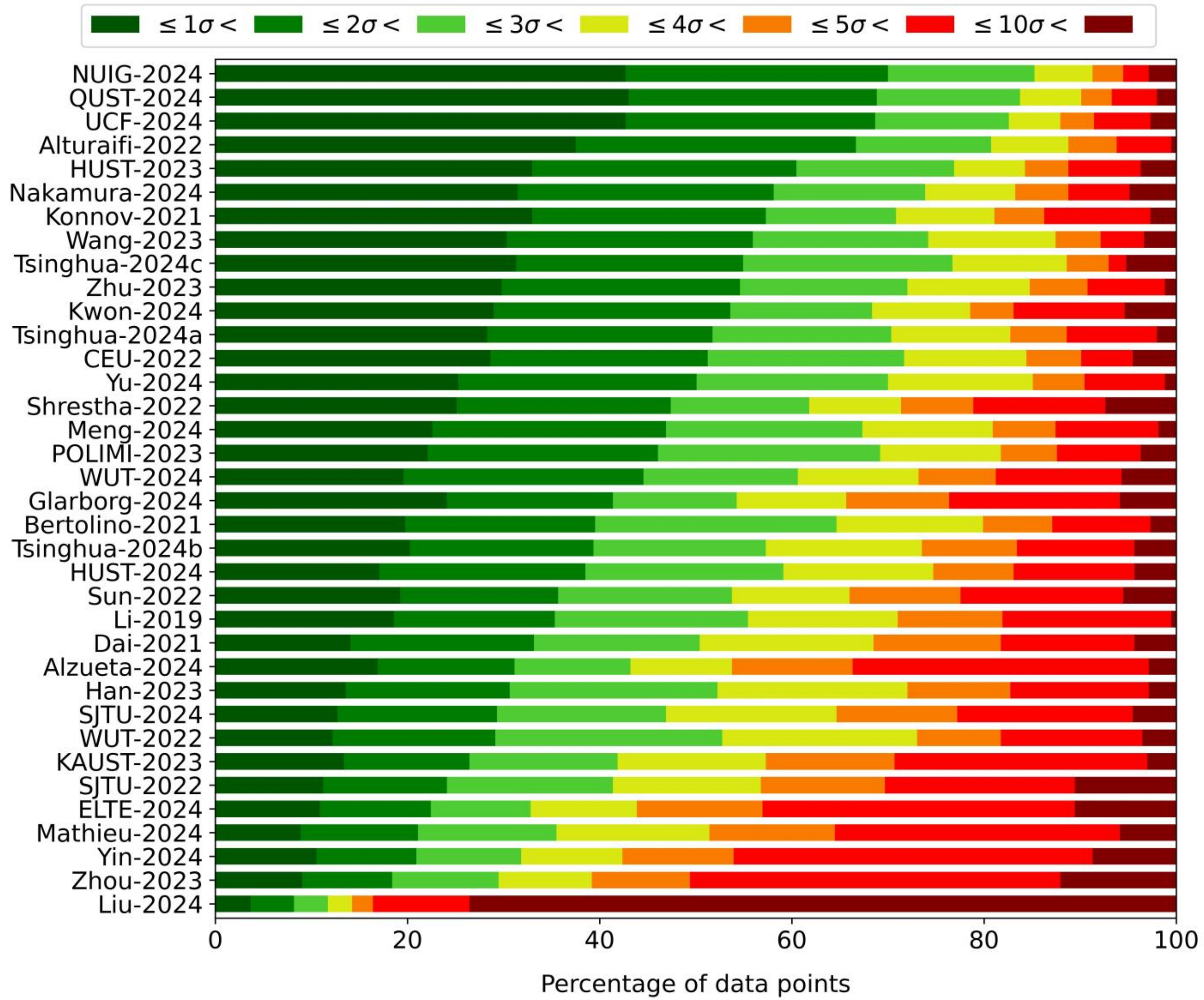
Stacked bar plots

Concentration data:



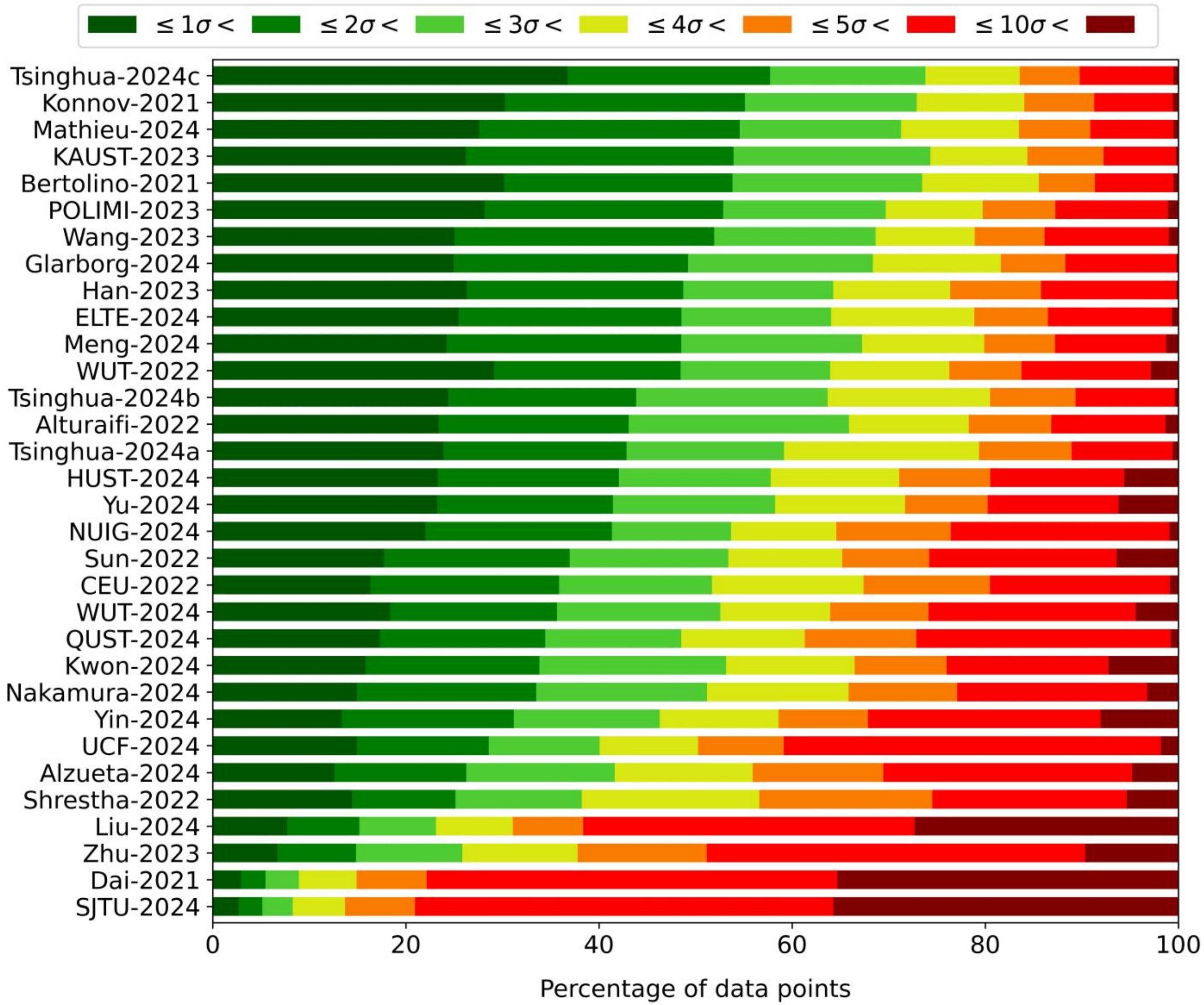
Stacked bar plots

IDT data:



Stacked bar plots

LBV data:



1. Introduction: What is mechanism validation?
2. Types of indirect experimental data used for mechanism validation
3. Frequently applied methods of mechanism validation
4. Quantitative mechanism validation using a squared error function
5. **Quantitative mechanism validation using curve matching (very briefly)**

Alessandro Stagni: Curve matching, Surface matching optimization
Wednesday (tomorrow), 12:20–13:20

Curve matching (CM)

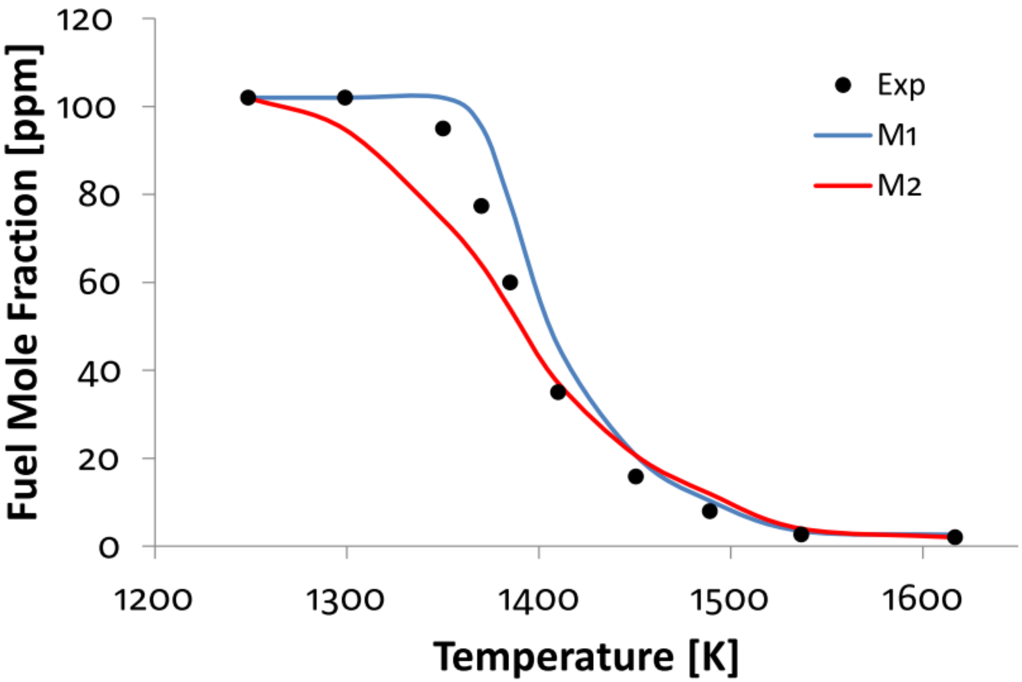
Previously discussed mechanism validation methods:
Pointwise agreement between the measured and simulated results was investigated.

CM approach [1]:
Data series of **discretely measured data points** and simulated results **are replaced by smooth, continuous curves** (*n* D functions) obtained by, e.g., spline interpolation.
The (dis)similarity between the two (measured and simulated) curves is investigated by various dissimilarity measures.

[1]: M. S. Bernardi, M. Pelucchi, A. Stagni, L. M. Sangalli, A. Cuoci, A. Frassoldati, P. Secchi, T. Faravelli, *Combust. Flame* 168 (2016) 186–203.

Curve matching (CM)

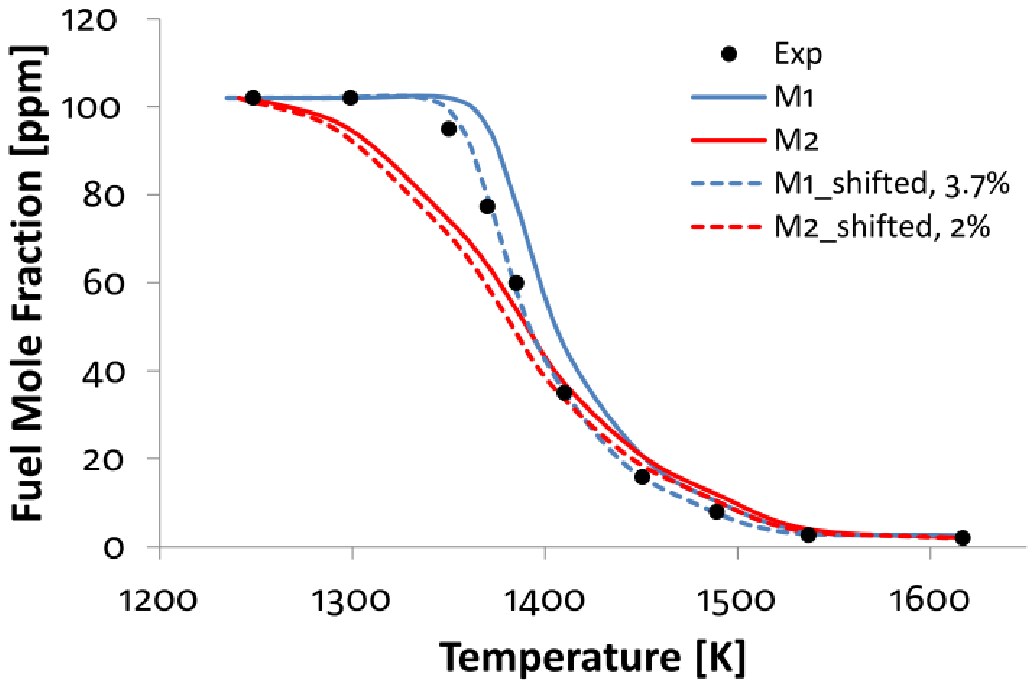
- The simulated curve may have the same shape as the experimental one but they are **shifted along the *x* axis** (may often occur for concentration profiles).
- Neither M1 or M2 predicts the onset *T* of the reaction accurately, but M1 predicts the shape of the curve better → **CM index accounts for the better shape**



M. S. Bernardi, M. Pelucchi, A. Stagni, L. M. Sangalli, A. Cuoci, A. Frassoldati, P. Secchi, T. Faravelli, *Combust. Flame* 168 (2016) 186–203.

Curve matching (CM)

- To eliminate the effect of horizontal shift, an **optimal horizontal shift is determined**
- **Dissimilarity indices are calculated for the shifted curves**



M. S. Bernardi, M. Pelucchi, A. Stagni, L. M. Sangalli, A. Cuoci, A. Frassoldati, P. Secchi, T. Faravelli, *Combust. Flame* 168 (2016) 186–203.

Curve matching (CM)

1. Data series are optimally shifted along the horizontal axis and the dissimilarity indices are calculated for the shifted curves

2. The dissimilarity indices are **normalized and combined to get an integrated index** → **CM index/score**

3. The **CM scores are averaged for many data series** to get an overall CM score for each mechanism
   → **experimental uncertainties** have to be considered (larger weights to more accurate experiments)

M. S. Bernardi, M. Pelucchi, A. Stagni, L. M. Sangalli, A. Cuoci, A. Frassoldati, P. Secchi, T. Faravelli, *Combust. Flame* 168 (2016) 186–203.

Curve matching (CM)

Example: NH_3 and NH_3/H_2 pyrolysis and combustion, thermal DeNOx

- The performance of **16 detailed mechanisms** was evaluated using the CM method
- Data collection: **5,201 data points in 435 data series** (IDT, LBV, concentration)

S. Girhe, A. Snackers, T. Lehmann, R. Langer, F. Loffredo, R. Glaznev, J. Beeckmann, H. Pitsch, *Combust. Flame 267* (2024) 113560.

Curve matching (CM)

Kinetic model	Species concentration						Ignition delay time	Laminar burning velocity	Overall mean
	Pyrolysis	Oxidation			Thermal $DeNO_x$	Mean			
		High *T*	Intermediate *T*	Low *T*					
NUIG_2023	0.947	0.941	0.860	0.889	0.865	0.900	0.930	0.876	0.902
KAUST_2023	0.951	0.901	0.872	0.884	0.869	0.895	0.914	0.884	0.898
KAUST_2021	0.951	0.902	0.872	0.886	0.859	0.894	0.915	0.882	0.897
POLIMI_2023	0.922	0.912	0.861	0.869	0.856	0.884	0.921	0.879	0.895
Mei_2021	0.899	0.930	0.862	0.844	0.872	0.881	0.921	0.880	0.894
Mei_2020	0.882	0.922	0.866	0.834	0.869	0.875	0.920	0.885	0.893
POLIMI_2020	0.941	0.891	0.863	0.854	0.842	0.878	0.917	0.882	0.893
Thomas_2022	0.911	0.929	0.857	0.843	0.854	0.879	0.918	0.879	0.892
POLIMI_2022	0.941	0.892	0.864	0.847	0.842	0.877	0.912	0.883	0.891
Marshall_2023	0.959	0.883	0.842	0.830	0.863	0.875	0.915	0.835	0.875
Han_2020	0.677	0.929	0.860	0.832	0.824	0.824	0.916	0.884	0.875
Manna_2022	0.931	0.900	0.876	0.837	0.865	0.882	0.911	0.827	0.873
Gotama_2022	0.848	0.910	0.848	0.836	0.707	0.830	0.911	0.872	0.871
Shrestha_2021	0.926	0.865	0.853	0.816	0.692	0.830	0.905	0.876	0.870
Glarborg_2018	0.872	0.887	0.841	0.833	0.859	0.859	0.915	0.809	0.861
Otomo_2018	0.924	0.805	0.832	0.833	0.756	0.830	0.910	0.816	0.852

0: no similarity – 1: perfect similarity

S. Girhe, A. Snackers, T. Lehmann, R. Langer, F. Loffredo, R. Glaznev, J. Beeckmann, H. Pitsch, *Combust. Flame 267* (2024) 113560.

E values vs. CM scores

CM scores

Kinetic model	Overall mean
NUIG_2023	0.902
KAUST_2023	0.898
KAUST_2021	0.897
POLIMI_2023	0.895
Mei_2021	0.894
Mei_2020	0.893
POLIMI_2020	0.893
Thomas_2022	0.892
POLIMI_2022	0.891
Marshall_2023	0.875
Han_2020	0.875
Manna_2022	0.873
Gotama_2022	0.871
Shrestha_2021	0.870
Glarborg_2018	0.861
Otomo_2018	0.852

E values

#	Mechanism	$\sqrt{E_{\text{overall}}}$
1	**NUIG-2024**	**4.7**
…		
6	**KAUST-2023**	**5.6**
…		
10	**POLIMI-2023**	**5.8**
…		
27	**CEU-2022**	**7.7**
…		

A. Gy. Szanthoffer, M. Papp, T. Nagy, T. Turányi, *Combust. Flame*, under review (2025)

S. Girhe, A. Snackers, T. Lehmann, R. Langer, F. Loffredo, R. Glaznev, J. Beeckmann, H. Pitsch, *Combust. Flame 267* (2024) 113560.

E values vs. CM scores

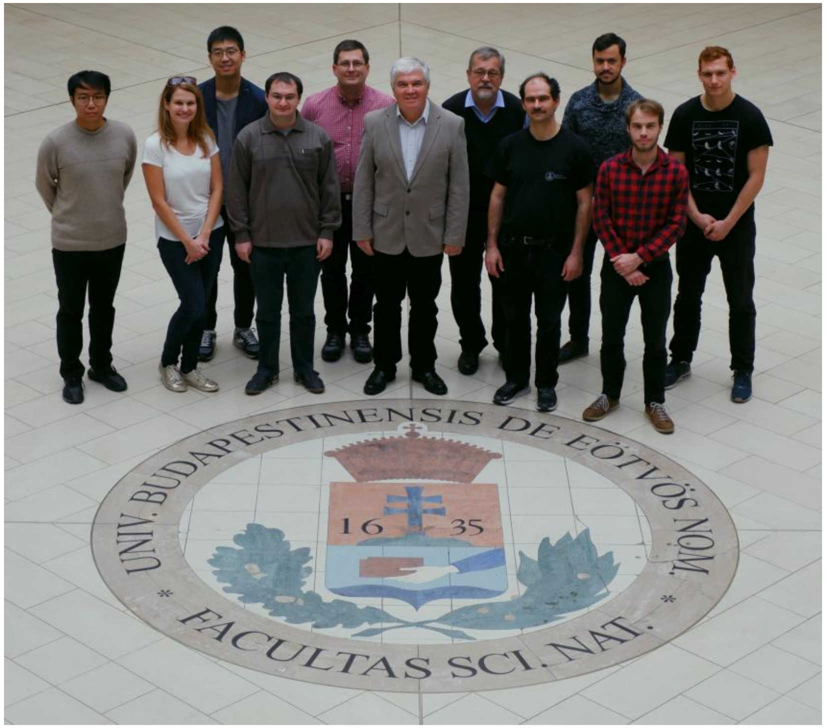
$\sqrt{E}$ value	CM score
Sensitive to the assigned experimental uncertainties (σ) → realistic estimation of the σ values is needed!	
Can easily be used for mechanism optimization	
Has exact statistical meaning – multiple of σ	Bootstrapping for statistics – can be used for the relative ranking of mechanisms
Based solely on the pointwise agreement between the experimental and simulated data, no smoothing or shifting is performed on the data	Based on the similarity of the shapes of the experimental and simulated data series fitted by smooth curves and optimally shifted horizontally

Practice on mechanism validation

András György Szanthoffer:
Using the Optima++ code for mechanism validation
Friday, 9:40–10:40

- Getting to know the Optima++ program facilitating mechanism validation
- Carrying out simulations using Optima++ and Cantera with various mechanisms
- Evaluating the performance of the investigated mechanisms using the squared error function with the help of Optima++

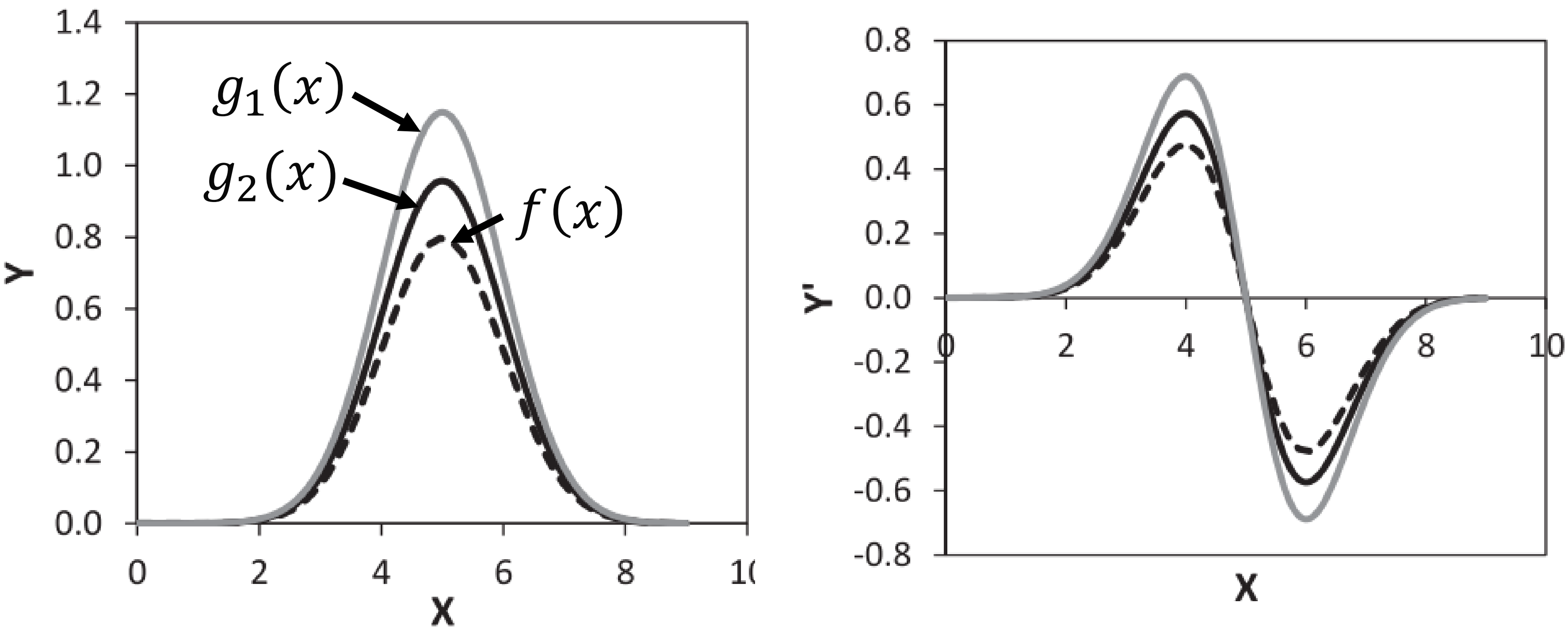
Thank you for your attention!



https://ChemKinLab.ELTE.hu

Curve matching (CM)

- $f(x), g(x)$: smoothed experimental and simulated data series as a function of variable x over the interval
- $f'(x), g'(x)$: first derivatives of $f(x), g(x)$



Curve matching (CM)

$$\|h\| = \sqrt{\int_D h(x)^2 dx}$$

L^2 norm of a function h over D

D: common domain of f and g

4 dissimilarity measures are defined:

$$d^0_{L^2}(f,g) = \frac{\|f-g\|}{|D|} \in (0,+\infty)$$

0 if f and g are the same (generalization of RMSE)

$$d^1_{L^2}(f,g) = \frac{\|f'-g'\|}{|D|} \in (0,+\infty)$$

0 if f and g differ only by vertical translation

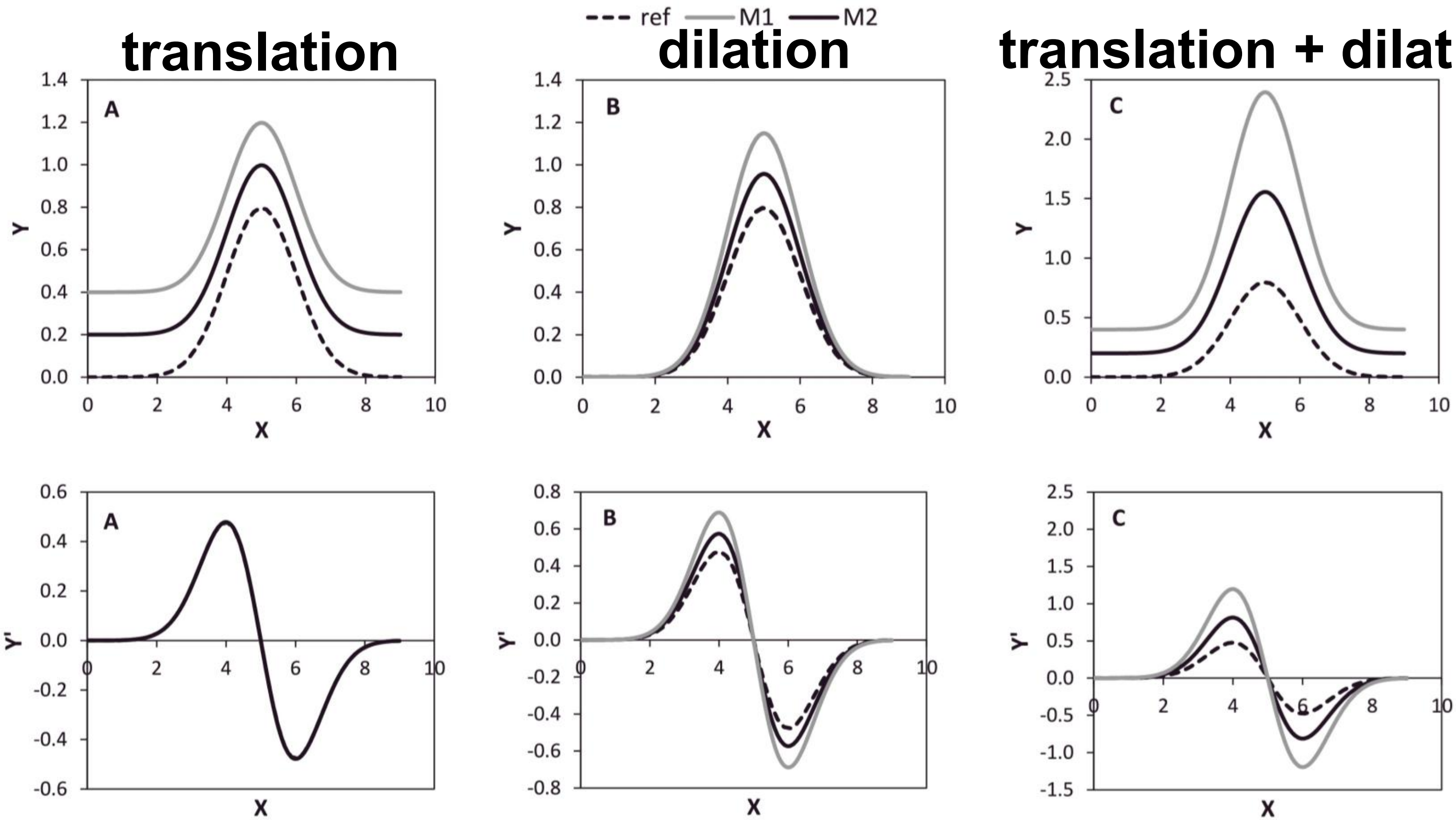
$$d^0_{Pearson}(f,g) = \frac{1}{2}\left\|\frac{f}{\|f\|} - \frac{g}{\|g\|}\right\| \in (0,1)$$

0 if f and g differ only by vertical dilation

$$d^1_{Pearson}(f,g) = \frac{1}{2}\left\|\frac{f'}{\|f'\|} - \frac{g'}{\|g'\|}\right\| \in (0,1)$$

0 if f and g differ only by vertical translation + dilation

Curve matching (CM)



	$d^0_{L^2}$	$d^1_{L^2}$	d^0_P	d^1_P		$d^0_{L^2}$	$d^1_{L^2}$	d^0_P	d^1_P		$d^0_{L^2}$	$d^1_{L^2}$	d^0_P	d^1_P
M_1	0.067	0.000	0.050	0.000	M_1	0.023	0.016	0.000	0.000	M_1	0.135	0.058	0.023	0.000
M_2	0.133	0.000	0.113	0.000	M_2	0.059	0.041	0.000	0.000	M_2	0.280	0.124	0.036	0.000