Reduction of kinetic reaction mechanisms I

Session 3-1

COST CM1404 Training School
Analysis, uncertainty quantification, validation, optimization and reduction of detailed combustion mechanisms for practical use of smart energy carriers

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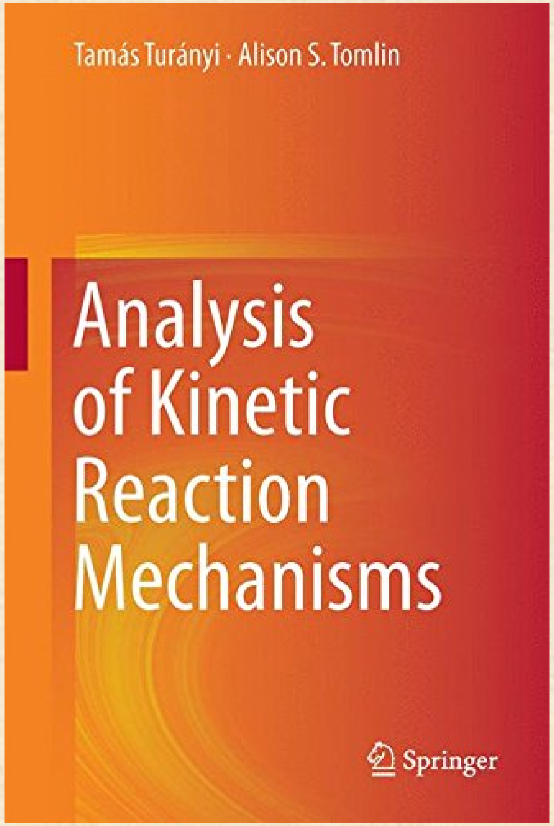
Analysis of kinetic reaction mechanisms

Tamás Turányi and Alison S. Tomlin:

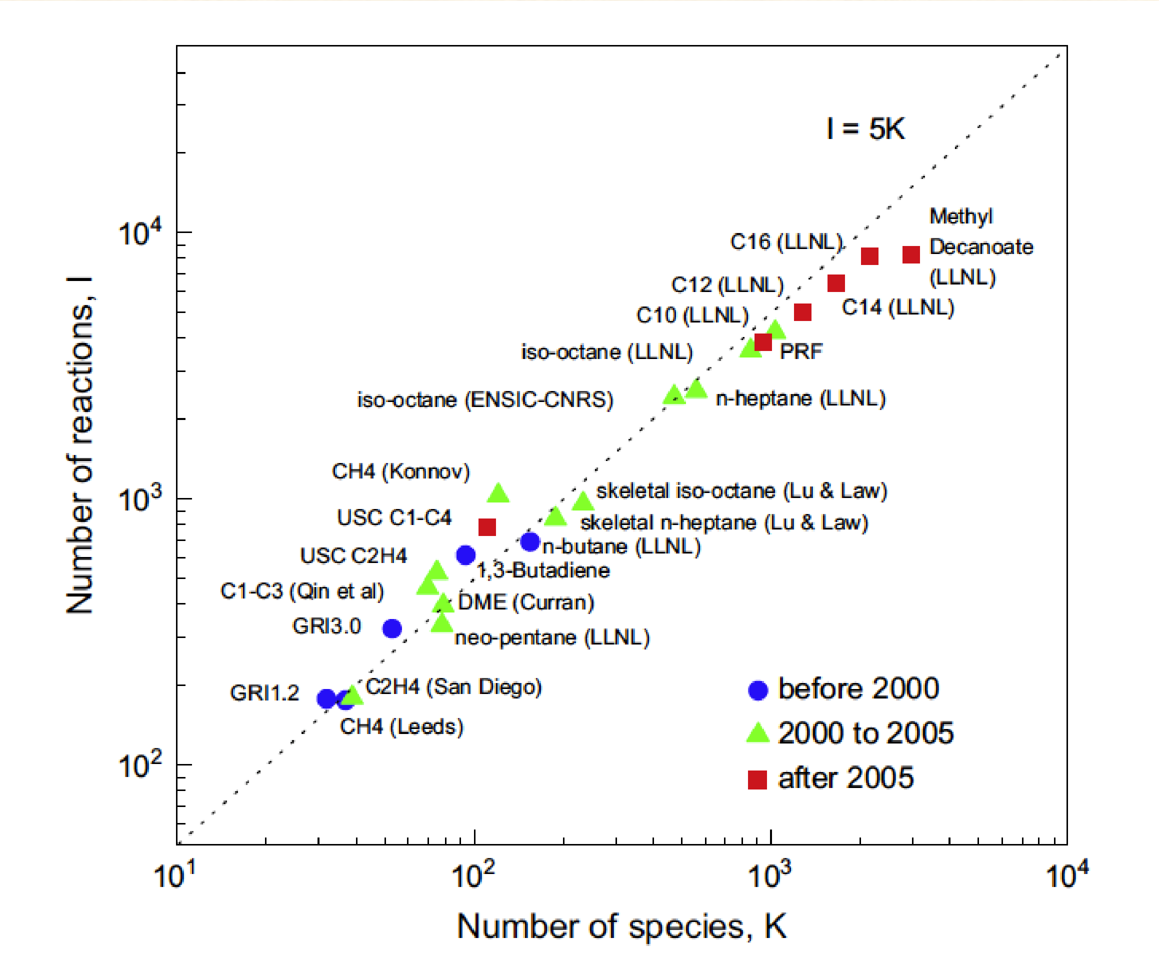
Analysis of kinetic reaction mechanisms

Springer, 2014

(with 1025 references)



Reaction mechanisms are getting larger



- **Increasing mechanistic and kinetic knowledge**
- **Rate rules** for quick or automatic construction
- **New systems explored** biofuels, surrogates
- **Hierarchical building** now allows huge models
  - biodiesel combustion
  - PAH formation
  - soot formation
- **Faster computers** allow their integration

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

Need for mechanism reduction

1 Spatially homogeneous system

$$\frac{\mathrm{d}\mathbf{c}(t)}{\mathrm{d}t} = \mathbf{f}(\mathbf{c}, T, p, \dots)$$

- ordinary differential equations (ODEs)
- large mechanism – **expensive** evaluation of the **right-hand side**
- **multiple timescales** (stiff systems)
  - ⇒ require **special integration techniques** (stiff ODE solvers)
- **the largest mech**-s can be integrated **within hours on a single core**

A skeletal model is needed to understand the chemistry.

2 Spatially inhomogeneous system

$$\frac{\partial\mathbf{c}(\mathbf{r}, t)}{\partial t} = \mathbf{f}(\mathbf{c}(\boldsymbol{r}, t), T(\boldsymbol{r}), p(\boldsymbol{r}), \mathbf{v}(\mathbf{r}), \dots)$$

- partial differential equations (PDEs)

- solved by **spatial discretization and operator splitting (chemi./transp.)** chemistry is solved at each timestep for each spatial unit. **most of the computer time (*e.g.* 99%)** is spent **on chemistry**.

- **practical limitation** in mechanism size **for 3D problems ~ 50 species**

Mechanism reduction speeds-up the calculations significantly and in many cases it makes it possible!

Overview of mechanism reduction methods

Mechanism reduction: giving a mathematically simplified, thus computationally more efficient description of the kinetic behaviour of the system.

I. Methods without considering time-scale separation

1. **skeletal mechanism reduction**
   elimination of redundant species and reactions
   ⇒ a smaller, less stiff ODE with mass-action kinetics
2. **lumping of species and reactions** (see in later sessions)
   combining similar species and reactions into ”lumped” ones

II. Methods based on time-scale separation (see in later sessions)

1. Simplification of the mechanism using methods QSSA, PEA, CSP
   ⇒ ODE for slow and algebraic equations for fast variables
2. slow manifold methods

III. Tabulated and fitted models (see in later sessions)

The various methods are often combined and
some methods can be applied repeatedly !

Possibility for skeletal reduction

Mechanisms usually contain redundant reactions/species

Developers try to remain on the safe side by adding most of the known species and reactions, some of which always turn out to be irrelevant at most of the conditions.

Application to a narrower range of conditions

The **domain of application** (T, p, **c** or φ range) is usually **smaller than** the **domain of validity of the original** mechanism.

Only some modelling results are of interest

For specific studies the reproduction of concentrations of **only some species or some features** (ignition delay, burning velocity) are of interest.

Some accuracy can be sacrificed

It is OK if due to reduction the simulation results change no more than the **error of the original mechanism & validation experiments** (say 10%).

Inhomogeneous systems ~ a series of homogeneous systems

Chemical conditions in inhomogeneous system can be covered by those in simpler 0D-1D systems (plug-flow reactors, PSRs, 1D laminar flames).

Various time scales are present (see in later sessions)

Original versus skeletal kinetic models

Even the original, detailed mechanisms are not „the real ones" !

They are rarely complete and general

- Several elementary **steps are ignored** due to **lack of** mechanistic or kinetic **knowledge**, **or** simply to **keep** their **size** within **tractable** limits.
- **Analytical and theoretical methods** often miss to find all species/steps.
- They have been created **for a given domain of conditions** (**c**, p, T).

They contain many uncertain parameters (see in later sessions)

- **rate coefficients** are often taken over from analogous reactions, and only a fraction of them are determined by accurate means.
- **transport parameters** are often handled alike.
- **thermodynamic data** can be rather uncertain **for larger species**

They are based on physical approximations

- **Ideal gas law** ($pV=nRT$) fails at high-pressure and when strong intermolecular forces are acting
- **Local thermal equilibrium approximation** (→ thermal rate coefficients) reaction products get thermalized before they react again

Basic notions in (skeletal) mechanism reduction

- **The aim of modelling**: the **accurate calculation of target quantities**
- **scenarios**: a **representative set of conditions** covering the domain of interest where some target quantities need to be reproduced with a desired accuracy with the reduced mechanism.
- **targets: important features**
  - ignition delay time
  - laminar flame speed
  - temperature profile, etc.
- **targets: concentration of important species**
  - major reactants, products, pollutants
  - some important intermediate (OH), etc.
- **necessary species and reactions**: those needed for the accurate calculation of targets (includes important species)
- **redundant species and reactions:** neither important and nor necessary, thus can be eliminated from the mechanisms

T. Turányi: Reduction of large reaction mechanisms, *New J.Chem.*, **14**, 795-803 (1990)

Skeletal reduction methods

There are around 50 methods for systematic skeletal reduction.

We will discuss some …

Species removal methods

1. **CM (1990)**: connectivity method (CM)
2. **DRG (2005)**: directed relation graph method
3. **DRGASA (2006)**: DRG-aided sensitivity analysis
4. **DRGEP (2007)**: DRG with error propagation
5. **PFA (2010)**: path flux analysis method (PFA)
6. **SEM-CM (2009)**: simulation error minimization connectivity method

Reaction removal methods

1. **ROPA (1970s):** rate of production analysis
2. **PCAS (1989)**: principal component analysis of the sensitivity matrix
3. **PCAF (1989)**: PCA of the rate sensitivity matrix
4. **SEM-PCAF (2009)**: PCAF with simulation error minimization

Removal of redundant species
Identification of necessary species

”Trial and error” based removal approach

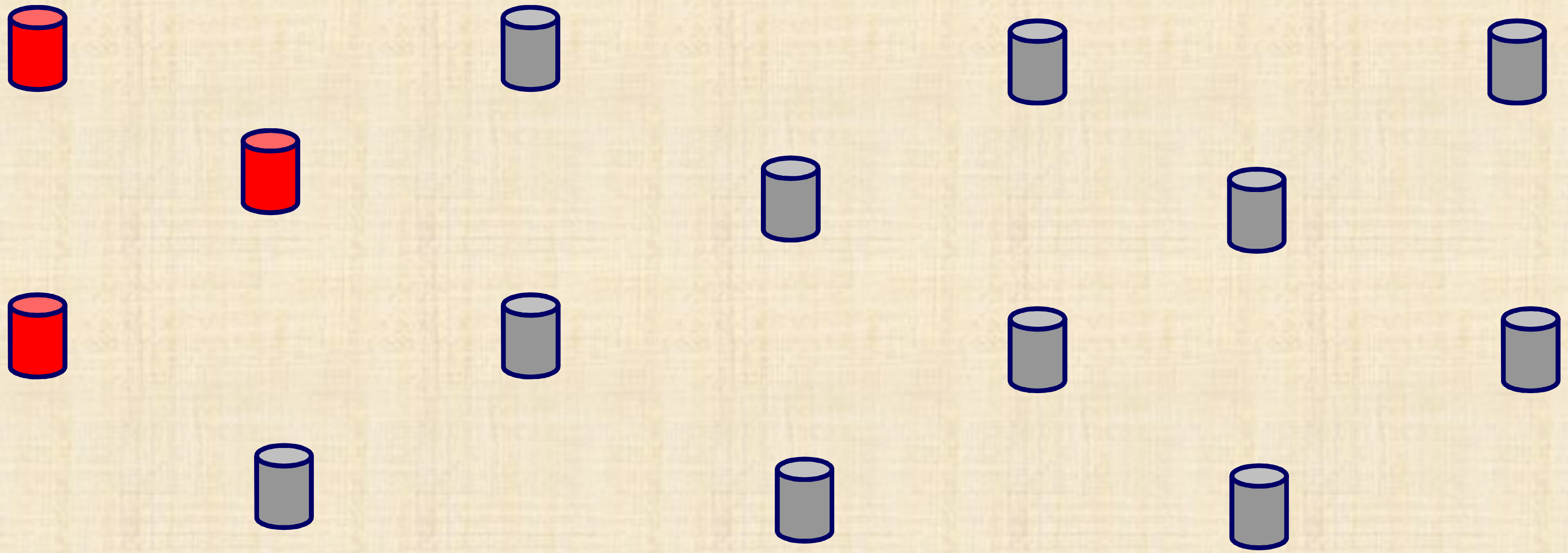
The **consuming reactions of each species is deleted one-by-one** and the **effect on targets is investigated with simulations**. **Not effective** enough as:

- **some species** can be eliminated **only in groups** *e.g.* those participating in fast preequilibrium reactions
- **elimination of species groups** ⇒ too many possibilities
- **very expensive for large mechanisms (e.g. number of species >300)**

”Kinetic connectivity” based building approach

1. Using a suitable measure **the ”kinetic connectivity” of each species to the group of already selected species** (initially the important ones) is determined
2. **Strongly connected species are selected.**
3. **Steps 1-2 are repeated until** the not yet selected species are all weakly linked to the group of necessary species.

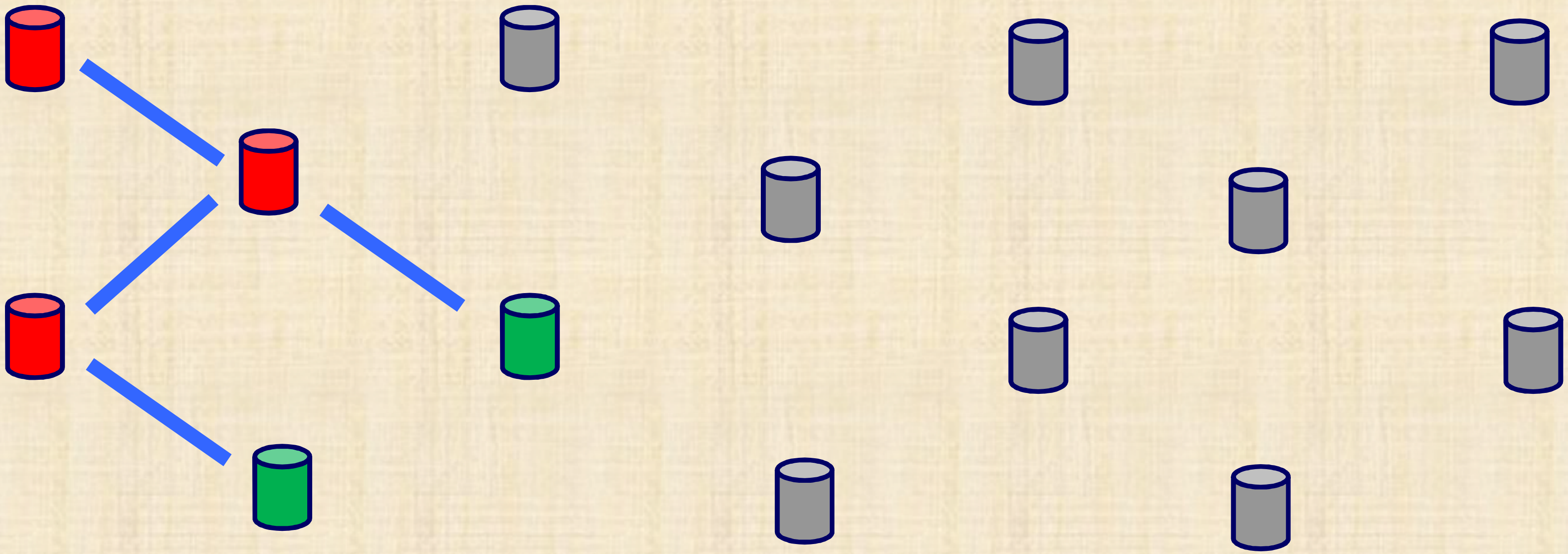
- **If the target is not a concentration** then it cannot be applied directly.



start

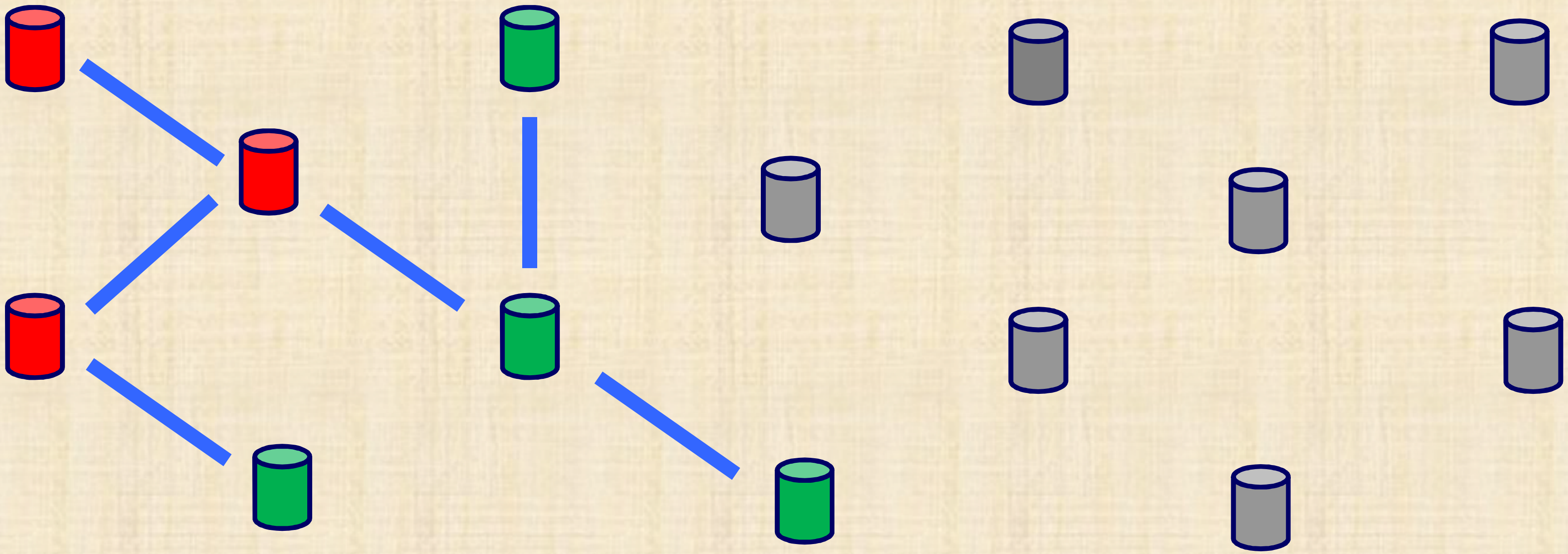
🟥 important species
= initally selected species

▨ not yet selected species



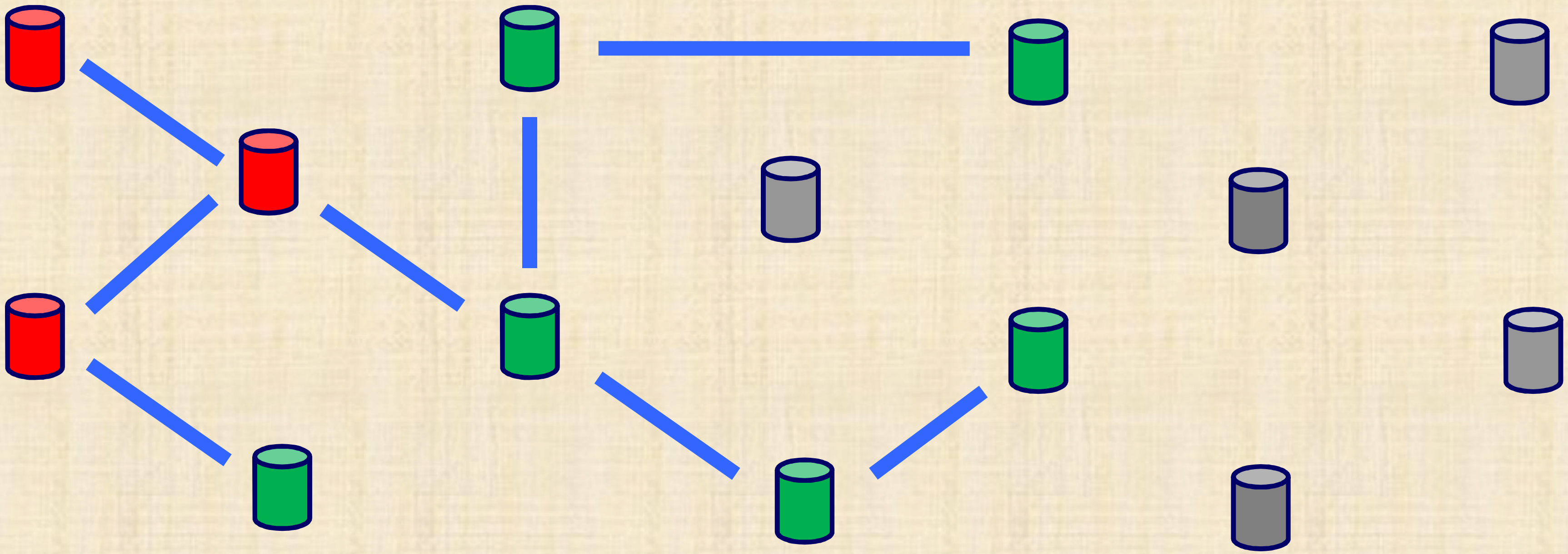
iteration 1

🟥 important species 🟩 necessary species ⬜ not yet selected species



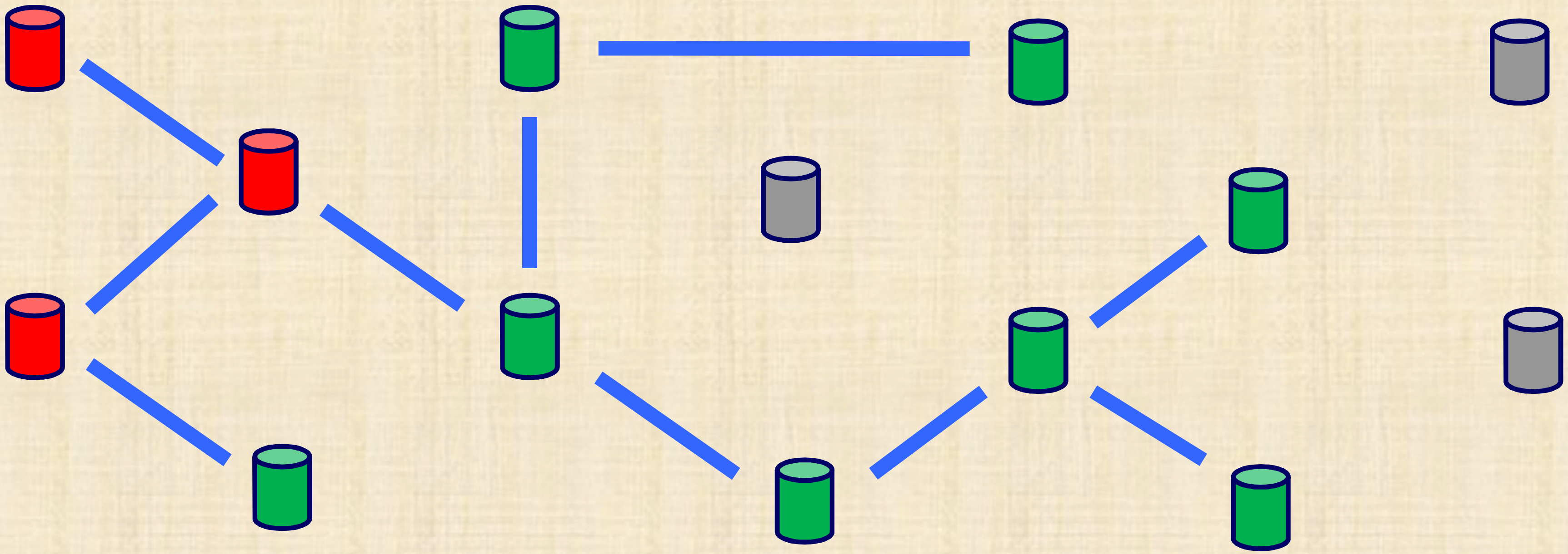
iteration 2

🟥 important species 🟩 necessary species ⬜ not yet selected species



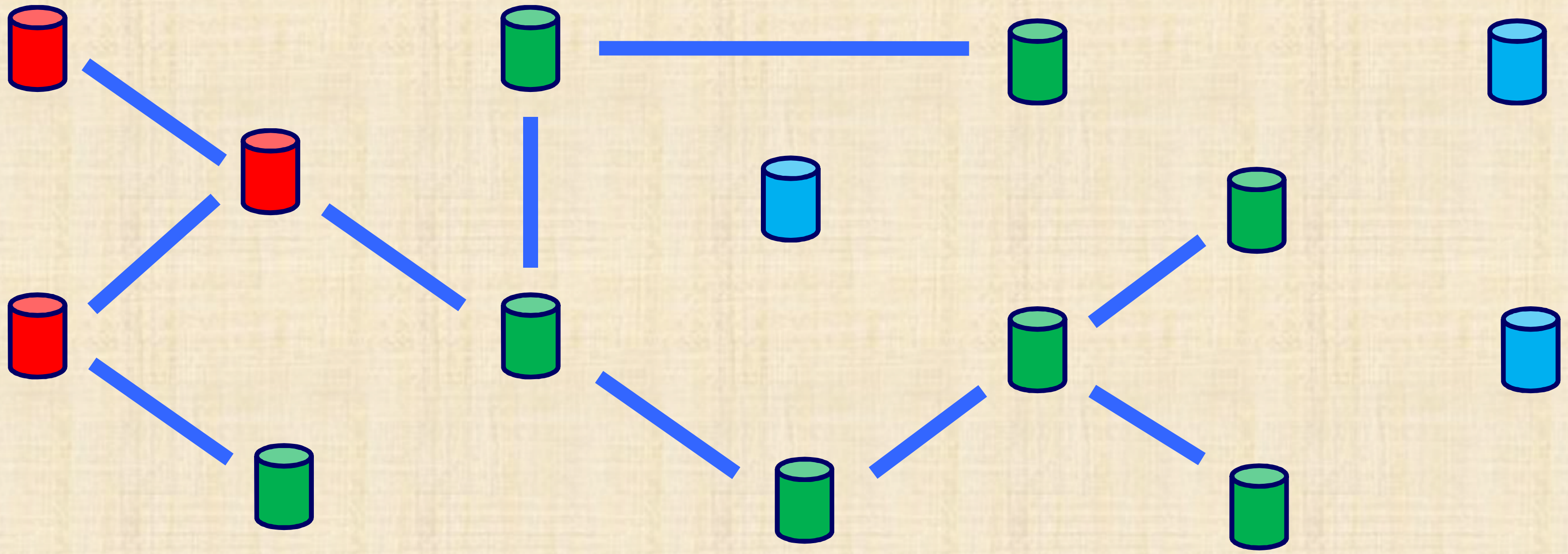
iteration 3

🟥 important species 🟩 necessary species ⬜ not yet selected species



iteration 4

🟥 important species 🟩 necessary species ⬜ not yet selected species



iteration 5

🟥 important species 🟩 necessary species 🟦 redundant species

Species removal 1: Connectivity Method (CM)

Kinetic connectivity of a species *i* to species *j*

is measured by the J_{ij} **element of the normalized Jacobian at a given time** (t_r):

$$\tilde{\mathbf{J}}_r = \left(\frac{\mathrm{d}\ln\mathbf{f}}{\mathrm{d}\ln\mathbf{c}}\right)_{t_r} = \left\{\tilde{J}_{ij}\right\} = \left\{\frac{\partial \ln f_\mathrm{j}}{\partial \ln c_\mathrm{i}}\right\} = \left\{\frac{c_\mathrm{i}}{f_\mathrm{j}}\frac{\partial f_\mathrm{j}}{\partial c_\mathrm{i}}\right\} \approx \left\{\frac{\Delta f_\mathrm{j}/f_\mathrm{j}}{\Delta c_\mathrm{i}/c_\mathrm{i}}\right\}$$

It shows the effect of a change in the concentration of species *i* on the production rate of species *j*.

Kinetic connectivity of species *i* to the group of selected species:

$$B_i = \sum_{\substack{j\text{:selected}\\ \text{species}}} \tilde{\mathbf{J}}_{ij}^2$$

- **All species ordered according to their B_i values.**
- Not yet selected **ones with "large" B_i values are selected**.
- The procedure **is repeated until a gap appears between the B_i values** of already selected and not yet selected species**.**
- **Repeated at each time t_r** and the **lists** of necessary species **are unified.**

T. Turányi: Reduction of large reaction mechanisms, *New J.Chem.*, **14**, 795-803 **(1990)**

Species removal 1: Connectivity Method (CM)

Advantages and disadvanteges

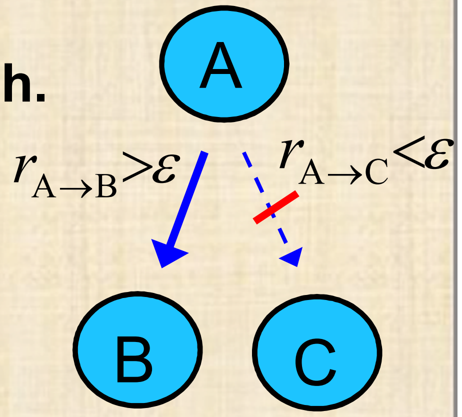
Advantages

- **simple and fast**
- available in **KINALC**
- **works well** for **small mechanisms**

Disadvantages

- The **threshold in B_i values** for stoppage **varies** from case to case.
- For mechanism with **large number of species** (>200), **no gap appears between the B_i values** of already selected and not-yet selected species.
- The **special role of important species diminishes with every step**.

Species Removal 2:
Directed Relation Graph (DRG) Method



- **The mechanism and the state is represented by a graph.**
- The **nodes** are the **species**
- Starting from **each target species** (e.g. A) a **directed edge is drawn to species B if B has a significant contribution to its production rate**.
- This effect is **measured by direct connection weight** $r_{\mathrm{A}\to\mathrm{B}}$

$$\boxed{r^{\mathrm{DRG}}_{\mathrm{A}\to\mathrm{B}} = \frac{\sum_{\substack{\alpha:\,\textbf{reactions}\\ \textbf{involving A\&B}}} \left|\nu_{\mathrm{A}\alpha} R^{\mathrm{net}}_{\alpha}\right|}{\sum_{\substack{\alpha:\,\textbf{reactions}\\ \textbf{involving A}}} \left|\nu_{\mathrm{A}\alpha} R^{\mathrm{net}}_{\alpha}\right|}}$$

$$R^{\mathrm{net}}_{\alpha} = R^{\mathrm{for}}_{\alpha} - R^{\mathrm{back}}_{\alpha} \ : \text{net rate of reac.}\ \alpha$$

$$\nu_{\mathrm{A}\alpha} \ : \text{stoich. num. of A in}\ \alpha$$

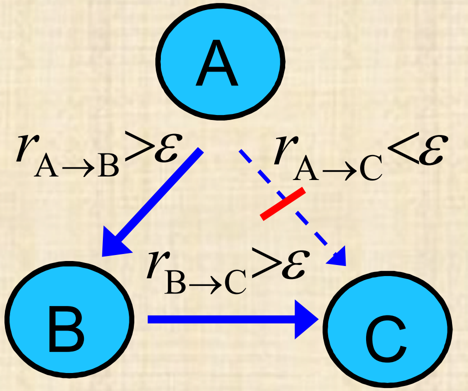
- $1 \geq r_{\mathrm{A}\to\mathrm{B}} \geq 0$ and $r_{\mathrm{A}\to\mathrm{A}} = 1$
- Species **B is necessary if** $\boxed{r_{\mathrm{A}\to\mathrm{B}} > \varepsilon}$
- **Threshold** ε is a small positive value (e.g. 0.1) given **by the modeler.**

T. Lu, C. K. Law: A directed relation graph method for mechanism reduction.
Proc. Comb. Inst., **30**, 1333–1341 (2005)

Species Removal 2:
Directed Relation Graph (DRG) Method

Selection procedure of necessary species

- **Iteratively** directed **edges are drawn from each newly selected species** (X) to other species (Y) **if $r_{X\to Y} > \varepsilon$** until no more vertices can be drawn.
- A **species is necessary** if there is **a directed path from a target species to it**.

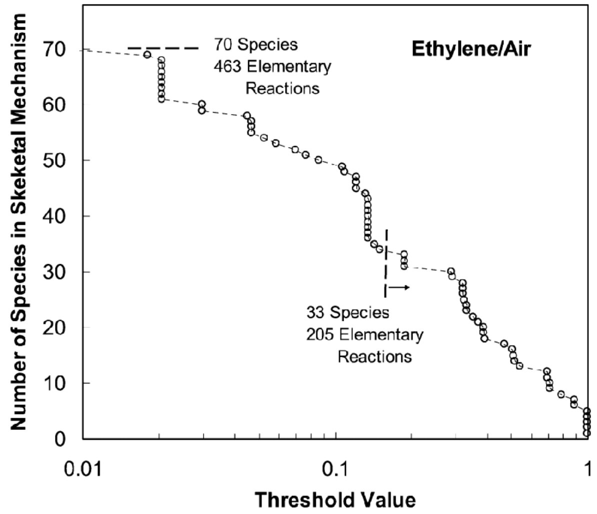


$$\varepsilon_C^{DRG} = \max(r_{A\to B}, r_{B\to C})$$

Importance of species C to the production of the target species (T_i) (critical value for selection)

$$\boxed{\varepsilon_C^{DRG} = \max_{T_i:\text{ targets}} \; \max_{\substack{P:\text{ paths} \\ T_i\to\ldots\to C}} \; \overbrace{\min_{XY\in P} r_{X\to Y}}^{\text{weakest link}}}$$

- **necessary** if $\boxed{\varepsilon_C > \varepsilon}$ and **redundant** if $\boxed{\varepsilon_C \le \varepsilon}$
- **Repeated at all selected times.**
- **Smaller ε** gives **larger** reduced **mechanism.**



Lu&Law: *Proc.Comb.Inst.*(2005)

Species Removal 2:
Directed Relation Graph (DRG) Method

"DRG with restart" method

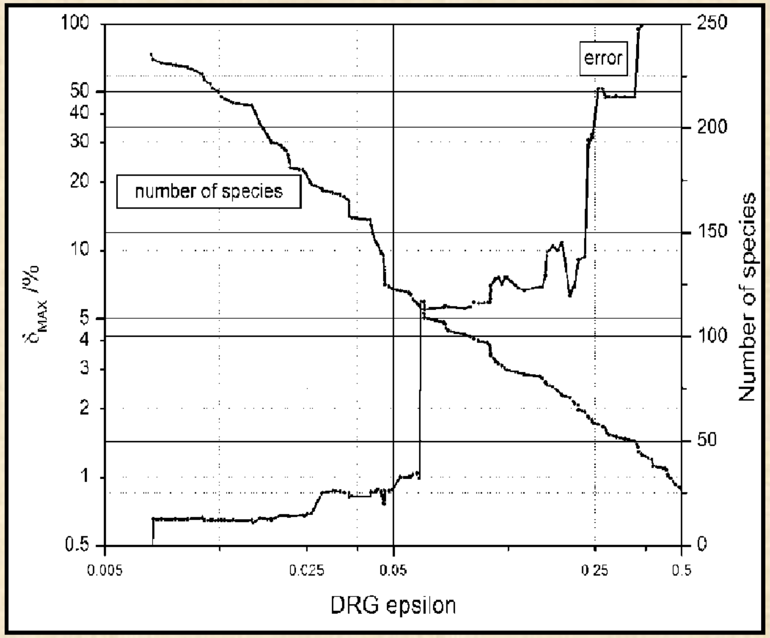
- **reapplying the DRG method to a DRG-reduced mechanism** (fluxes have changed !)
- **Often a smaller reduced mechanism can be obtained at a given accuracy.**

DRG method is simple & fast

⇒ widespread

But, it is suboptimal because

- **Every selected** species becomes **equally important.**
- **Rates** of all selected species are **reproduced even when they are small.**
- **Simulation error** does **not** decrease **monotonically** with decreasing ε



T.Nagy, T.Turányi Combust. Flame. (2009)

T. Lu, C. K. Law: Linear time reduction of large kinetic mechanisms with directed relation graph: *n*-heptane and *iso*-octane. *Combust. Flame*, **144** 24–36 (2006)

Species Removal 3:
DRG-Aided Sensitivity Analysis (DRGASA) Method

DRG-reduced mechanisms usually still contain redundant species

- which have only **minor effect on the targets species or features**
- even though they **might have more significant effect on other species**

Identifying such redundant species

- **Elimination of a single species at a time** and **compute** the induced **error**.
- **Similar to sensitivity-analysis**, but it evaluates the effect of a **big change**.
- **DRG-aided: only species with low critical ε^{DRG} value**, which is above threshold ε by a little, are **tested**

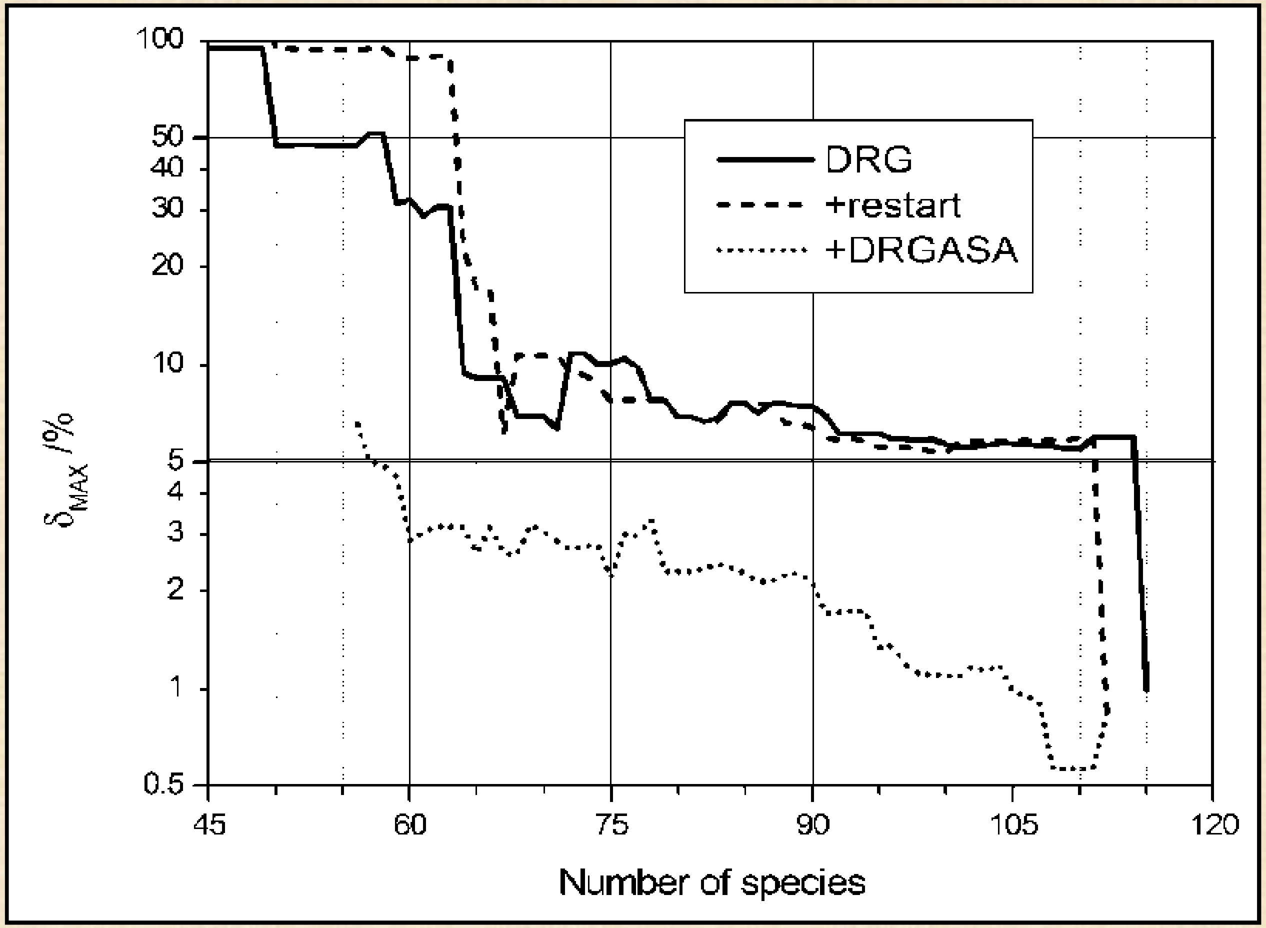
  e.g. species in the range of $0.2 = \varepsilon \leq \varepsilon^{DRG} \leq 0.4$ are investigated
- The **error** induced by species removal is **determined for each** species.
- The **species** whose removal causes **the smallest error is removed.**
- The **procedure is repeated** until the error becomes unacceptably large.

X.L. Zheng, T.F. Lu, C.K. Law: Experimental counterflow ignition temperatures and reaction mechanisms of 1,3-butadiene, *Proc. Comb. Inst.*, **31**, 367–375 (2007)

DRG vs. DRG with restart vs. DRGASA methods

Case study: reduction of a methane partial oxidation mechanism

- **full mechanism**: 6874 reaction, **345 species**
- **aim**: 5% maximum error in the concentration profile of 12 target species



DRG with restart

- **slighlty better** results with repeated application

DRGASA

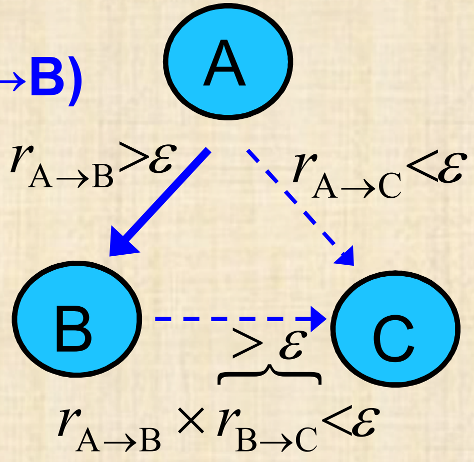
- started from a mechanism with 1% accuracy

⇒ **much smaller mechanism** at 5% error

T. Nagy, T. Turányi: Reduction of very large reaction mechanisms using methods based on simulation error minimization, *Combust. Flame*, **156** 417–428 (2009)

Species Removal 4: Directed Relation Graph with Error Propagation (DRGEP) method

DRGEP definition of the weight of directed vertices (A→B)



$$r^{\mathrm{DRGEP}}_{\mathrm{A\to B}} = \frac{\left|\sum_{\substack{\alpha:\,\text{reactions}\\ \text{involving A\&B}}} \nu_{\mathrm{A}\alpha} R^{\mathrm{net}}_{\alpha}\right|}{\max\left(\sum_{\substack{\alpha:\,\text{reactions}\\ \text{producing A}}} \underbrace{(\nu_{\mathrm{A}\alpha} R^{\mathrm{net}}_{\alpha})}_{>0},\ -\sum_{\substack{\alpha:\,\text{reactions}\\ \text{consuming A}}} \underbrace{(\nu_{\mathrm{A}\alpha} R^{\mathrm{net}}_{\alpha})}_{<0}\right)}$$

It measures the ratio of sum of the production rates of species A from reactions involving B to the maximum of the total formation or destruction rates of A.

Importance of C to the target species (*T*$_i$) (critical value for selection)

$$\varepsilon^{\mathrm{DRGEP}}_{\mathrm{C}} = \max_{\mathrm{T}_i:\,\text{targets}} \ \max_{\substack{\mathrm{P:\,paths}\\ \mathrm{T}_i\to\ldots\to\mathrm{C}}} \underbrace{\prod_{\mathrm{XY}\in\mathrm{P}} r^{\mathrm{DRGEP}}_{\mathrm{X\to Y}}}_{\text{product over direct links}}$$

$$\varepsilon^{\mathrm{DRGEP}}_{\mathrm{C}} = \max(r^{\mathrm{DRGEP}}_{\mathrm{A\to B}} \times r^{\mathrm{DRGEP}}_{\mathrm{B\to C}}, r^{\mathrm{DRGEP}}_{\mathrm{A\to C}})$$

C is not selected!

- Species C is **necessary** if $\boxed{\varepsilon_C > \varepsilon}$ and **redundant** if $\boxed{\varepsilon_C \le \varepsilon}$
- **Better than DRG, as selected species don't become equally important.**

P. Pepiot-Desjardins, H. Pitsch: An efficient error-propagation-based reduction method for large chemical kinetic mechanisms, *Combust. Flame*, **154**, 67-81 (2008)

Species Removal 5: Path Flux Analysis (PFA)

- **Production (P_A) and consumption (C_A) fluxes** of species *A*:

$$P_{\mathrm{A}} = \sum_{\substack{\alpha:\textbf{reactions}\\ \textbf{producing A}}} \underbrace{\left(\nu_{\mathrm{A}\alpha} R_\alpha^{\mathrm{net}}\right)}_{>0} \qquad C_{\mathrm{A}} = \sum_{\substack{\alpha:\textbf{reactions}\\ \textbf{consuming A}}} \underbrace{\left(\nu_{\mathrm{A}\alpha} R_\alpha^{\mathrm{net}}\right)}_{<0}$$

- Production (P_{AB}) and consumption (C_{AB}) fluxes of species A **via species B**

$$P_{\mathrm{A\to B}} = \sum_{\substack{\alpha:\textbf{reactions}\\ \textbf{producing A}\\ \textbf{involving B}}} \underbrace{\left(\nu_{\mathrm{A}\alpha} R_\alpha^{\mathrm{net}}\right)}_{>0} \qquad C_{\mathrm{A\to B}} = \sum_{\substack{\alpha:\textbf{reactions}\\ \textbf{consuming A}\\ \textbf{involving B}}} \underbrace{\left(\nu_{\mathrm{A}\alpha} R_\alpha^{\mathrm{net}}\right)}_{<0}$$

- The **1st and 2nd generation flux ratios separately for the production and consumption**:

$$r_{\mathrm{A\to B}}^{\mathrm{prod-1st}} = \frac{P_{\mathrm{AB}}}{\max\left(P_{\mathrm{A}}, C_{\mathrm{A}}\right)} \qquad r_{\mathrm{A\to B}}^{\mathrm{con-1st}} = \frac{C_{\mathrm{AB}}}{\max\left(P_{\mathrm{A}}, C_{\mathrm{A}}\right)}$$

$$r_{\mathrm{A\to B}}^{\mathrm{prod-2nd}} = \sum_{\mathrm{M}_i \neq \mathrm{A,B}} r_{\mathrm{A}M_i}^{\mathrm{prod-1st}} r_{M_i\mathrm{B}}^{\mathrm{prod-1st}} \qquad r_{\mathrm{A\to B}}^{\mathrm{cons-2nd}} = \sum_{\mathrm{M}_i \neq \mathrm{A,B}} r_{\mathrm{A}M_i}^{\mathrm{cons-1st}} r_{M_i\mathrm{B}}^{\mathrm{cons-1st}}$$

- **Total effect:**

$$\boxed{\varepsilon_{\mathrm{A\to B}}^{\mathrm{PFA}} = r_{\mathrm{A\to B}}^{\mathrm{prod-1st}} + r_{\mathrm{A\to B}}^{\mathrm{cons-1st}} + r_{\mathrm{A\to B}}^{\mathrm{prod-2nd}} + r_{\mathrm{A\to B}}^{\mathrm{cons-2nd}} \quad \text{(+optionally higher-order terms)}}$$

- Starting from the important species, using relation $\boxed{\varepsilon_{\mathrm{A\to B}} > \varepsilon}$ the set of further necessary species are identified. Even more effective than DRGEP.

W. T. Sun, Z. Chen, X. L. Gou, Y. G. Ju: A path flux analysis method for the reduction of detailed chemical kinetic mechanisms *Combust. Flame* **157**, 1298-1307 (2010)

Common features of the DRG/DRGEP/PFA/CM methods

- All are based on **the investigation of the system of kinetic ODEs.**
- **INPUT: list of important species:**

  Optimal choice of species for global targets (IDT, T_{fin})**?**
- **INPUT: a threshold value** (B_i or ε) controls the mechanism size, but

  It is **not directly related to the simulation error**, especially when targets are global properties (e.g. ignition delay time).
- Only **few reduced mechanisms** are produced and **tested in simulations.**
- However, homogeneous **modelling with small mechanisms is very fast !**

Concept of ”simulation error minimization (SEM)”

During the skeletal mechanism building procedure **use simulation error as a guide to selecting** those **species** from strongly connected ones whose inclusion to the mechanism reduces the error in the steepest manner !

T. Nagy, T. Turányi: Reduction of very large reaction mechanisms using methods based on simulation error minimization, *Combust. Flame*, **156** 417–428 (2009)

Improving on the connectivity method (CM)

- assume a **two-step** mechanism: 1. **A** + B → C $c_{A,0}=c_{D,0}>0$

  2. **D** → B $c_{B,0}=c_{C,0}=0$
- **important species: A ⇒ expectation**: both reactions are necessary
- **rule: a reaction is selected, if all of its species are necessary**

CM cycle 1: selects only B (but not C), **thus no reaction is selected !**

”Empty mechanism”

⇒ a complementary set: ”the unit of selecting species”

a single or a group of not yet selected **species**, **whose inclusion** into the mechanism results in the selection of **at least one additional reaction.**

modified CM cycle 1:

- both B, C are selected**, but there is no forming route to species B !**

”Dead mechanism”

⇒ a living species: **”an essential requirement”**

has **nonzero initial** concentration **or** an **inflow** term (e.g. in PSR) **or** there is a **formation route** in the reduced mechanism from such species

living or consistent reduced mechanism: all of its species are living

Species Removal 5: Simulation error minimization connectivity method (SEM-CM)

1. Initiation

- definition of **scenarios** and running **simulations** with the full mechanism
- selection of the **representative time points** both **for reduction** and **for error calculation** of local properties
- **saving concentration sets** and lognormed **Jacobians** at these points
- **providing** the **important properties** or **species** whose simulation with the reduced mechanism should fulfill the **accuracy requirements**.

2. Identification of complementary sets

- For the group of currently selected species **complementary sets of species are determined** by going through all reactions and deleting all selected species.
- These sets **may contain each other or overlap**.

T. Nagy, T. Turányi: Reduction of very large reaction mechanisms using methods based on simulation error minimization, *Combust. Flame*, **156**, 417–428 (2009)

Species Removal 6: SEM-CM

3. Ranking the complementary sets

according to their **average strength of the direct link** to the group of selected species is, which is characterized by C_k for complementary set k :

$$C_k = \frac{1}{n_k} \sum_{\substack{\text{species } j \text{ in} \\ \text{compl.set } k}} B_j = \frac{1}{n_k} \sum_{\substack{\text{species } j \text{ in} \\ \text{compl.set } k}} \sum_{\substack{\text{selected} \\ \text{species i}}} \tilde{\mathbf{J}}_{ij}^2$$

4. Generation of several extended sets

- **extended set:** adding a complementary set to the selected species
- **several** complementary sets **with similarly strong link** (C_k) exist
- **depth level *m*:** **each** complementary sets **down to the *m*-th in the rankings** are added to the mechanism resulting in ***m* extended sets**.

Species Removal 6: SEM-CM

5. Generation of living reduced mechanisms

- extended sets obtained at a reaction time **may contain non-living species**
- **complementary sets of the forming reactions of non-living species** are determined at the current and earlier times within the scenario.
- **Maximum values of lognormed Jacobian elements** at these times are used for **ranking** these complementary sets:

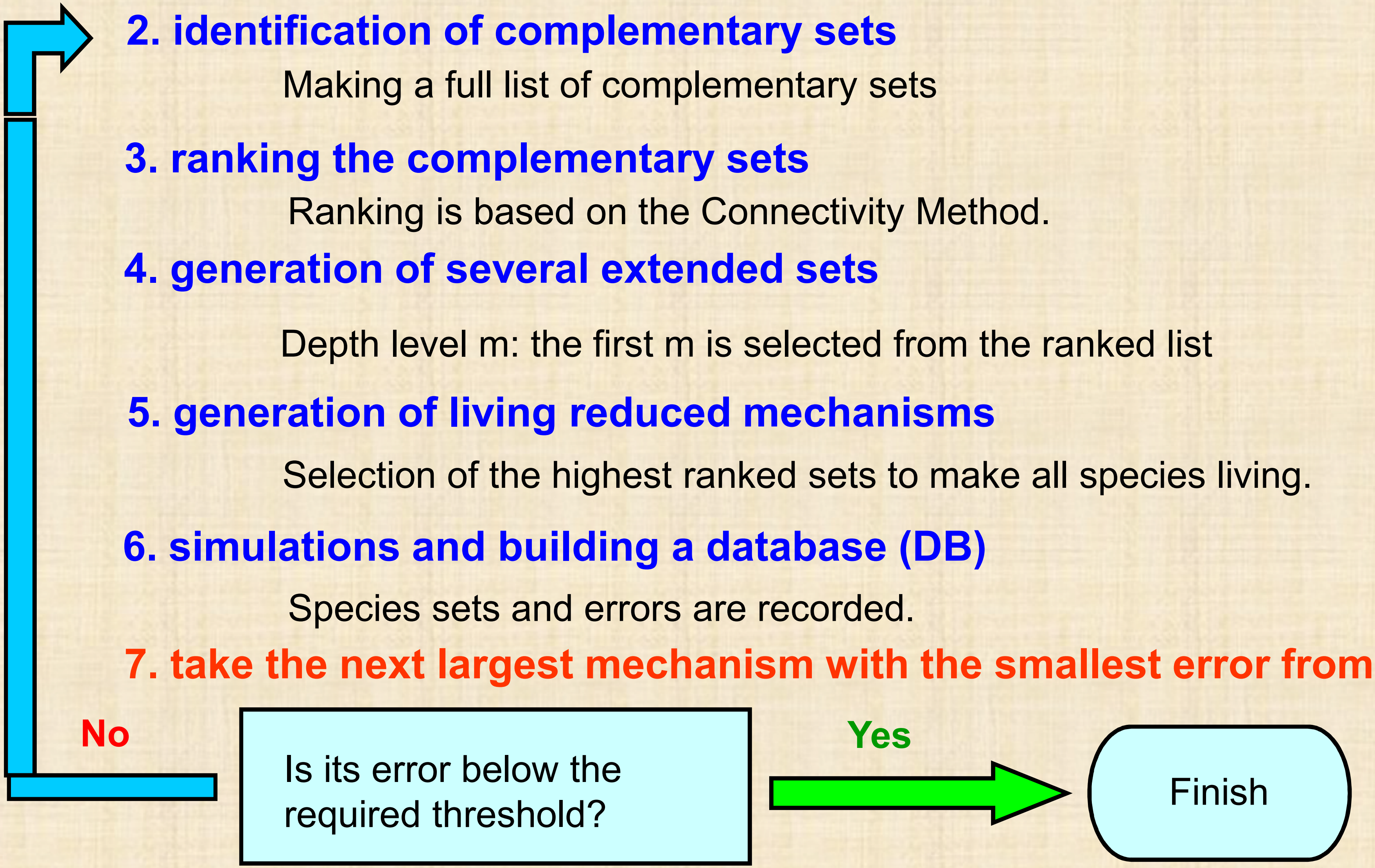
$$\overline{C}_k = \frac{1}{n_k} \sum_{\substack{\text{species } j \text{ in} \\ \text{compl.set } k}} \overline{B}_{\mathrm{j}} = \frac{1}{n_k} \sum_{\substack{\text{species } j \text{ in} \\ \text{compl.set } k}} \sum_{\substack{i:\text{non-living} \\ \textbf{selected} \text{ species}}} \tilde{J}^2_{\max,ij}(t_k) \qquad \tilde{J}^2_{\max,ij}(t_k) = \max_{l:\, t_l < t_k} \tilde{J}^2_{ij}(t_l)$$

- **Highest ranked** complementary sets are **added** and the procedure is repeated **until all** species become **living**.

6. Simulations and building a database

- **Each** generated **living reduced mechanism** is **simulated** in **all scenarios**, unless they have been simulated before.
- **Species lists** and **simulation errors** are **stored** in a database.

Species Removal 6: SEM-CM



1. initiation

Simulations with the full mechanism, saving **c** and **J**

2. identification of complementary sets

Making a full list of complementary sets

3. ranking the complementary sets

Ranking is based on the Connectivity Method.

4. generation of several extended sets

Depth level m: the first m is selected from the ranked list

5. generation of living reduced mechanisms

Selection of the highest ranked sets to make all species living.

6. simulations and building a database (DB)

Species sets and errors are recorded.

7. take the next largest mechanism with the smallest error from DB

No

Is its error below the required threshold?

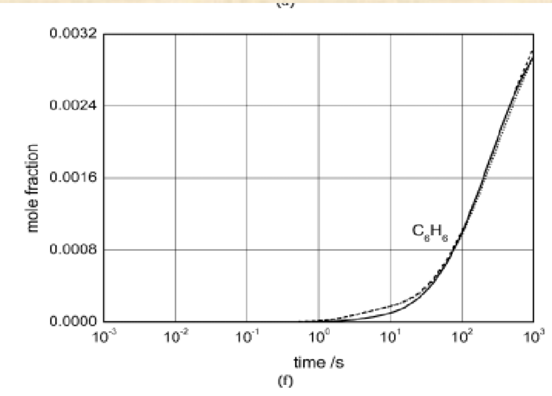
Yes

Finish

SEM case study 1: gas-phase chemistry in solid-oxide fuel cells (SOFC): partial oxidation of methane

- **Dean et al. mechanism:** 345 species and 6874 irreversible reactions.
- Reduction is needed **for computer optimization of fuel cell geometry and operating conditions.**
- typical conditions: ***T* = 900˚C, *p* =1 atm, isothermal and isobaric**
- **30 / 70 vol% methane / air**
- **12 important species**: CH_4, N_2, O_2, H_2, H_2O, CH_2O, CO, CO_2, C_2H_2, C_2H_4, C_2H_6, C_6H_6. ($x_{max} > 0.001$)
- Aim: **concentration error < 5% for 1000s** simulation time
- **Mixed error** of species *i* at time t_j

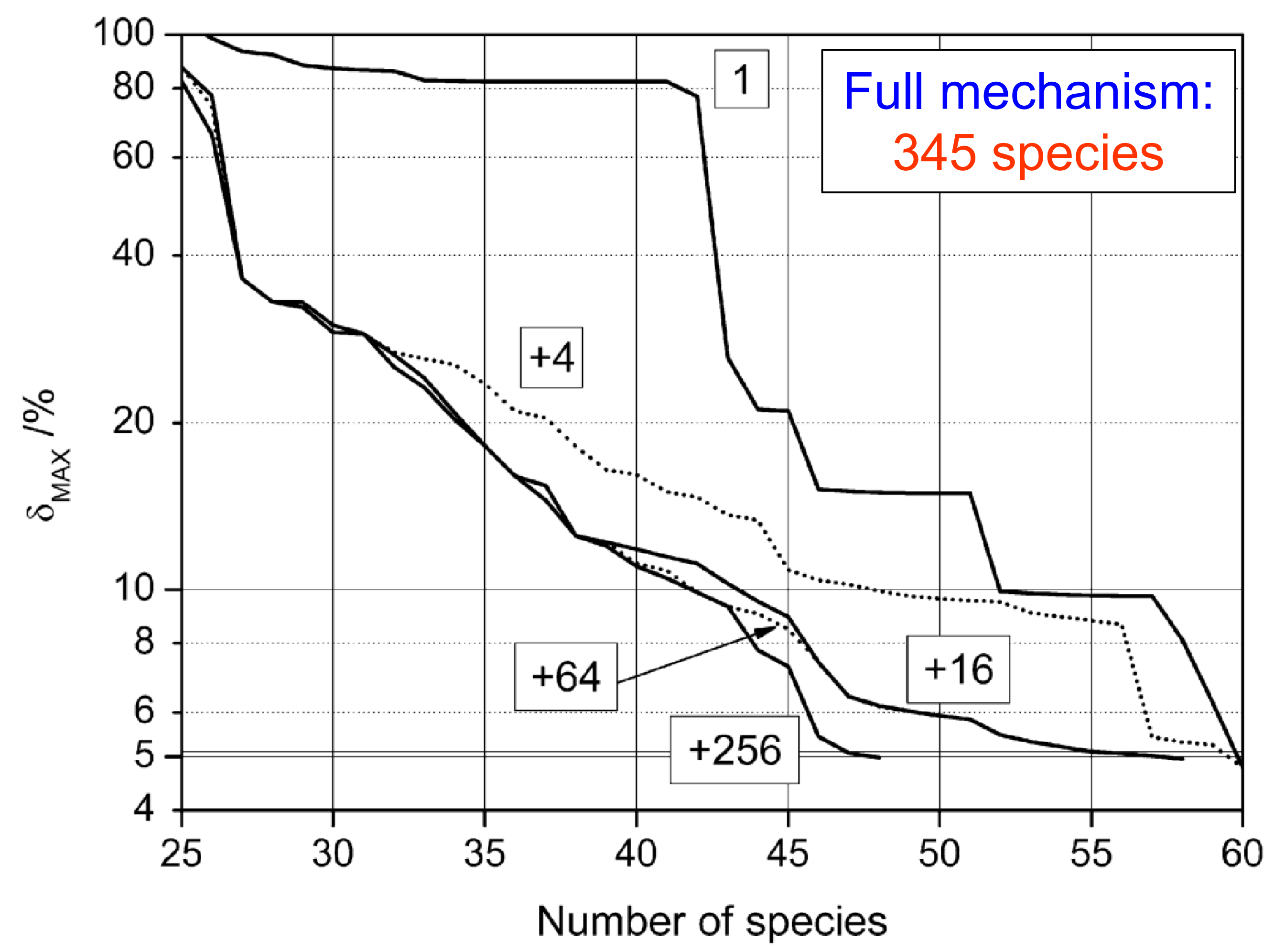
$$\delta_i(t_j) = 2\frac{c_i^{\text{red}}(t_j) - c_i^{\text{full}}(t_j)}{c_i^{\text{full}}(t_j) - c_{i,\text{MAX}}^{\text{full}}} \approx \begin{cases} \dfrac{c_i^{\text{red}}(t_j) - c_i^{\text{full}}(t_j)}{c_i^{\text{full}}(t_j)} & \text{if } c_i^{\text{full}}(t_j) \sim c_{i,\text{MAX}}^{\text{full}} \\ \dfrac{c_i^{\text{red}}(t_j) - c_i^{\text{full}}(t_j)}{c_{i,\text{MAX}}^{\text{full}}/2} & \text{if } c_i^{\text{full}}(t_j) << c_{i,\text{MAX}}^{\text{full}} \end{cases}$$



- **Worst case error** considering all times and species

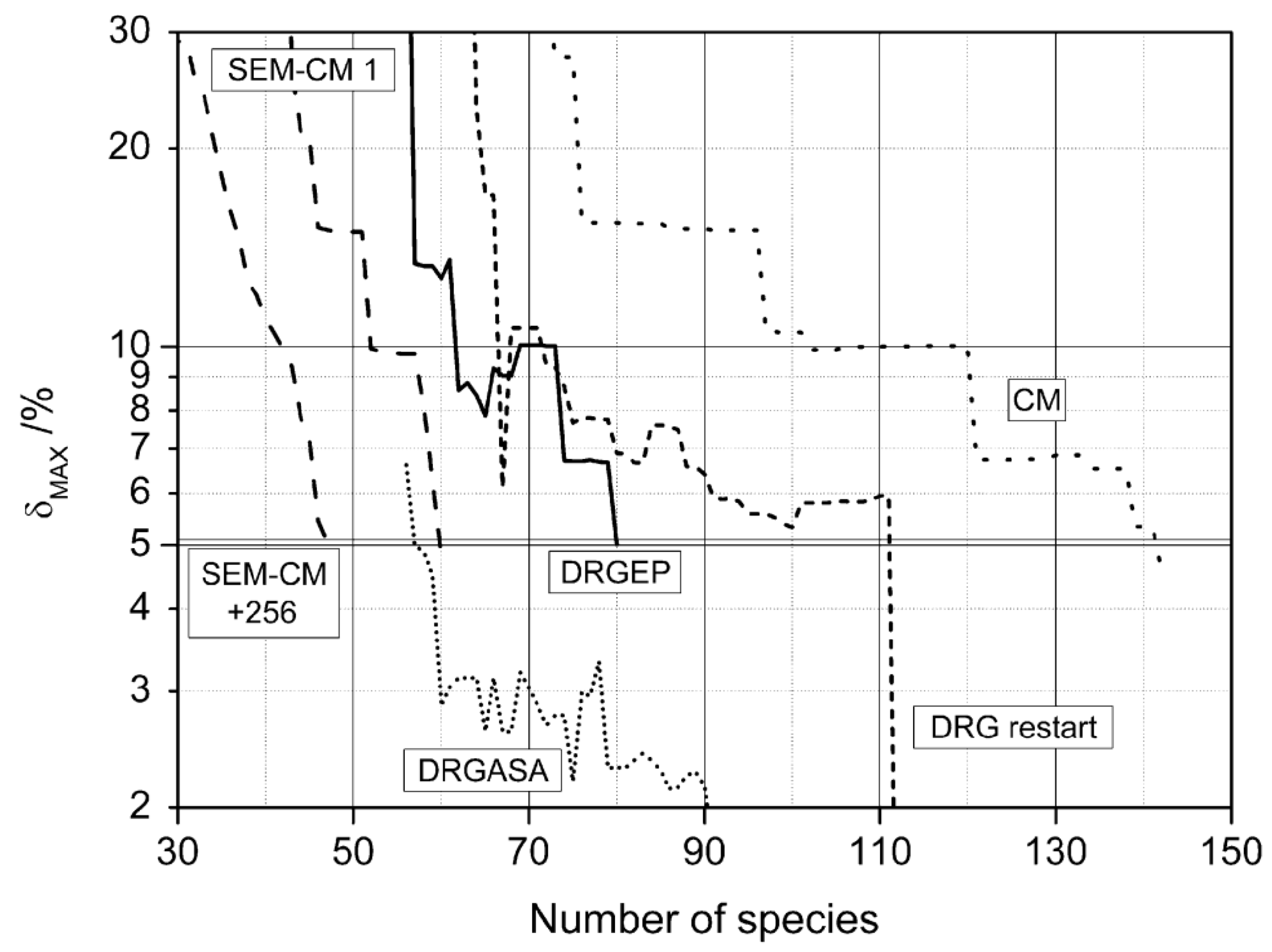
$$\delta_{\text{MAX}} = \max_i \max_j \left| \delta_i(t_j) \right|$$

SEM case study 1: gas-phase chemistry in solid-oxide fuel cells (SOFC): partial oxidation of methane



Repeated (same full mech!) with increasing depth level of 1,4,16,64, 256 using previously stored databases ⇒ **cannot worsen**!

SEM case study 1: gas-phase chemistry in solid-oxide fuel cells (SOFC): partial oxidation of methane



Method time
(8 years ago!)

DRG+restart+
DRGASA
~10 min

DRGEP
~1 min

CM
~1 min

SEM-CM *m*=1
~12 min

SEM-CM..*+256*
10.5h

SEM case study 1: gas-phase chemistry in solid-oxide fuel cells (SOFC): partial oxidation of methane

mechanism	**species**	**reactions**	**speed-up**
original	345	6874	1×
CM	139	2494	6×
DRGEP	80	1172	21×
DRG+restart+DRGASA	57	821	38×
SEM-CM	47	613	58×

Simulation time scales squarely with the species number
⇒ The SEM-CM reduced mechanism allows the fastest simulations.

These mechanisms usually still contain **redundant reactions**:
⇒ **reaction removal** methods are applied for further reduction.

T. Nagy, T. Turányi: Reduction of very large reaction mechanisms using methods based on simulation error minimization, *Combust. Flame*, **156**, 417–428 (2009)

Reaction removal 1:
The classic rate-of-production analysis (ROPA)

The **contribution** of each reaction step **to the formation and removal of each necessary species** is investigated at several time points.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \underbrace{+k_2 ya + k_4 xa}_{\text{all formation terms}} \quad \underbrace{-k_1 xy - 2k_3 x^2 - 0{,}5k_5 xy}_{\text{all consumption terms}}$$

measure of contribution:

$$\boxed{r_{\mathrm{A}\beta} = \begin{cases} \nu_{\mathrm{A}\beta} R_\beta \Big/ \sum_{\substack{\alpha:\text{ reactions}\\ \text{producing A}}} (\underbrace{\nu_{\mathrm{A}\alpha}}_{>0} R_\alpha) & \text{if } \nu_{\mathrm{A}\beta} > 0 \\ \nu_{\mathrm{A}\beta} R_\beta \Big/ \sum_{\substack{\alpha:\text{ reactions}\\ \text{consuming A}}} (\underbrace{\nu_{\mathrm{A}\alpha}}_{<0} R_\alpha) & \text{if } \nu_{\mathrm{A}\beta} < 0 \end{cases}}$$

$$R_\alpha \text{ : rate of an elementary step (one-way), always} > 0$$

- **A reaction β can be eliminated, if its contribution is less than a little threshold value ε to all species at all investigated times.**

$$\varepsilon_\beta = \max_{\text{times } t_i} \ \max_{\text{all species A}} \ r_{\mathrm{A}\beta}(t_i) < \varepsilon \qquad \text{e.g.} \quad \varepsilon = 0.05$$

Reaction removal 1:
The classic rate-of-production analysis (ROPA)

KINALC output

$$f_{\mathrm{A}} = \sum_{\alpha} \nu_{\mathrm{A}\alpha} R_{\alpha}^{\mathrm{net}}$$

Net production rate = formation – consumption

$r_{\mathrm{A}\beta}$(%) < ε = 5%

$r_{\mathrm{A}\beta}$(%)

```
CH4                   Rate :   -1.082E-08
        No    Contribution                #   reaction

         1    -1.17547E-08   34.8 %C   152   C2H3+CH4 => C2H4+CH3
         2     9.13403E-09   39.8 %P   151   C2H4+CH3 => C2H3+CH4
         3    -7.16821E-09   21.2 %C   140   CH≡CCH2.+CH4 => CH≡CCH3+CH3
         4    -5.71162E-09   16.9 %C   136   CH2=CHCH2.+CH4 => CH2=CHCH3+CH3
         5     3.72978E-09   16.2 %P   139   CH≡CCH3+CH3 => CH≡CCH2.+CH4
         6     3.60756E-09   15.7 %P   135   CH2=CHCH3+CH3 => CH2=CHCH2.+CH4
         7     3.45436E-09   15.0 %P   143   C2H6+CH3 => C2H5+CH4

CH3                   Rate :    4.636E-10
        No    Contribution                #   reaction

         1    -1.69871E-08   22.7 %C     7   2CH3 => C2H6
         2     1.17547E-08   15.6 %P   152   C2H3+CH4 => C2H4+CH3
         3    -9.13403E-09   12.2 %C   151   C2H4+CH3 => C2H3+CH4
         4     7.84580E-09   10.4 %P     8   C2H6 => 2CH3

C2H2                  Rate :    1.996E-09
        No    Contribution                #   reaction

         1     6.06561E-09   44.1 %P    81   CH2=CHCH2. => C2H2+CH3
         2    -5.12527E-09   43.6 %C    82   C2H2+CH3 => CH2=CHCH2.
         3     3.86101E-09   28.1 %P   190   C2H3(+M) => H+C2H2(+M)
         4    -3.15073E-09   26.8 %C   189   H+C2H2(+M) => C2H3(+M)
         5    -1.15098E-09    9.8 %C    67   C2H2+CH3 => CH≡CCH3+H
```

Reaction removal 2: Principal Component Analysis of the Concentration Sensitivity Matrix (PCAS)

The normalized local sensitivity matrix $\tilde{\mathbf{S}}_r$ is calculated at several time points (*r*=1,..,*n*) in a **time interval** :

$$\tilde{\mathbf{S}}_r = \frac{\mathrm{d}\ln\mathbf{c}(t_r)}{\mathrm{d}\ln\mathbf{k}} = \left\{\frac{k_j}{c_i}\frac{\partial c_i(t_r)}{\partial k_j}\right\} \qquad \Rightarrow \textbf{for the period:} \quad \tilde{\mathbf{S}} = \begin{bmatrix} \tilde{\mathbf{S}}_1 \\ \vdots \\ \tilde{\mathbf{S}}_n \end{bmatrix}$$

c_i: conc. of spec. i $\quad k_j$: rate coef. of reac. j

PCA requires the eigenvector-eigenvalue decomposition of matrix $\tilde{\mathbf{S}}^{\mathrm{T}}\tilde{\mathbf{S}}$

$$\sum_{r=1}^{n}\sum_{i:\text{species}} \left|\Delta\ln c_i(t_r)\right|^2 \overset{\varepsilon<<1}{\approx} \Delta\ln\mathbf{k}^{\mathrm{T}} \cdot \overbrace{\underbrace{\tilde{\mathbf{S}}^{\mathrm{T}}\tilde{\mathbf{S}}}_{n_{\text{reac}}\times n_{\text{reac}}}}^{\mathbf{U}\Lambda\mathbf{U}^{\mathrm{T}}} \cdot \overbrace{\Delta\ln\mathbf{k}}^{(\varepsilon,..,\varepsilon)^{\mathrm{T}}} \overset{\text{PCA}}{>\approx} \varepsilon^2 \sum_{\lambda_j>\lambda_{\text{th.}}} \overbrace{\lambda_j}^{>0} \sum_{|u_{jk}|>u_{\text{th.}}} u_{jk}^2$$

- $\tilde{\mathbf{S}}^{\mathrm{T}}\tilde{\mathbf{S}}$ is sym. positive definite, **U** unitary, Λ diagonal
- **large components of eigenvector u**$_j$ designates **connected reactions**,
- **large eigenvalues** λ_j belongs to **the important reaction groups**.

A reaction step *j* is important if it belongs to at least one important reaction group, that is it has a large component ($|u_{jk}|>u_{\text{thres.}}$) in an eigenvector with a large eigenvalue ($\lambda_{jk}>\lambda_{\text{thres.}}$).

Reaction removal 3: Principal Component Analysis of the Rate Sensitivity Matrix (PCAF)

The normalized local rate sensitivity matrix $\tilde{\mathbf{F}}_r$ is calculated at several time points (r=1,..,n):

$$\tilde{\mathbf{F}}_r = \left(\frac{\mathrm{d}\ln\mathbf{f}}{\mathrm{d}\ln\mathbf{k}}\right)_{t_r} = \left\{\frac{k_j}{f_i}\frac{\partial f_i(t_r)}{\partial k_j}\right\}_{t_r} = \left\{\frac{\nu_{ij}R_j}{f_i}\right\}_{t_r}$$

f_i: rate of prod. of spec. i

R_j: rate of reac. j

ν_{ij}: stoich.num. of spec. i

PCA requires the eigenvector-eigenvalue decomposition of matrix $\tilde{\mathbf{F}}_r^{\mathrm{T}}\tilde{\mathbf{F}}_r$

$$\sum_{i:\text{species}} \left|\Delta\ln f_i(t_r)\right|^2 \overset{\varepsilon<<1}{\approx} \Delta\ln\mathbf{k}^{\mathrm{T}} \cdot \underbrace{\overbrace{\tilde{\mathbf{F}}_r^{\mathrm{T}}\tilde{\mathbf{F}}_r}^{\mathbf{U\Lambda U}^{\mathrm{T}}}}_{n_{\text{reac}}\times n_{\text{reac}}} \cdot \overbrace{\Delta\ln\mathbf{k}}^{(\varepsilon,..,\varepsilon)^{\mathrm{T}}} \overset{\text{PCA}}{>\approx} \varepsilon^2 \sum_{\lambda_j>\lambda_{\text{th.}}} \overbrace{\lambda_j}^{>0} \sum_{|u_{jk}|>u_{\text{th.}}} u_{jk}^2$$

- $\tilde{\mathbf{F}}_r^{\mathrm{T}}\tilde{\mathbf{F}}_r$ is sym. positive definite, **U** unitary, Λ diagonal
- **large components of eigenvector u**$_j$ designates **connected reactions**,
- **large eigenvalues** λ_j belongs to **the important reaction groups**.

A reaction step is important if it belongs to at least one important reaction group at at least one of timepoints.

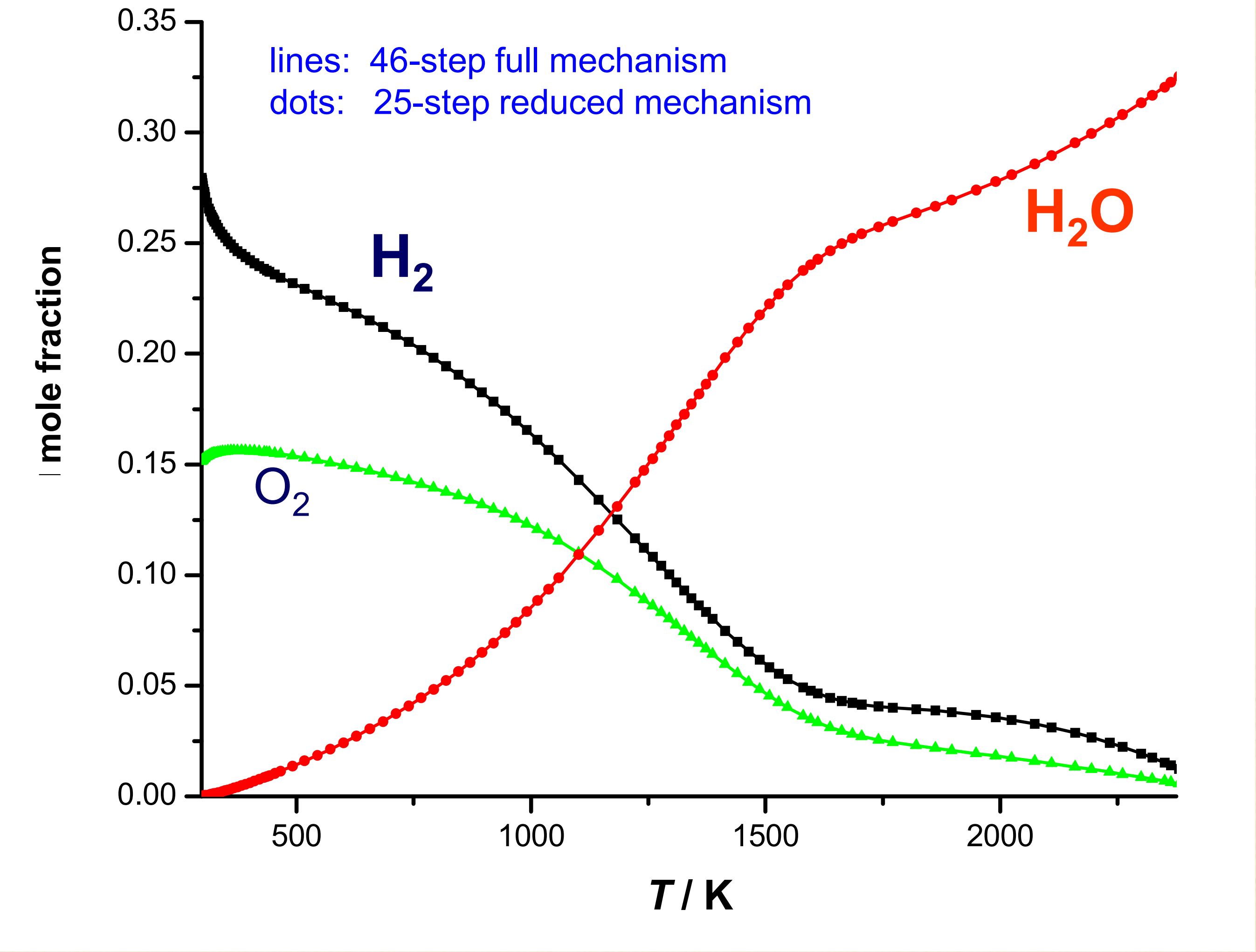
T. Turányi, T. Bérces, S. Vajda: Reaction rate analysis of complex kinetics systems
Int.J.Chem.Kinet., **21,** 83-99 **(1989)**

PCAS versus PCAF

PCAS	**PCAF**
• investigation of **sensitivity functions**, which depend **on the prehistory** of the simulation	• investigation of **reaction rates**, which depend **on the actual concentrations** only
• analysis belongs to **a time interval**	• analysis **in time points**
• **direct inspection of the change of simulation results on parameter perturbation (**parameter estimation)	• **change of importance of reactions** in time can be investigated
• **S** calculated **numerically**	• **F** calculated **analytically**

In all investigated cases PCAS and PCAF provided exactly the same reduced mechanisms.

Case study: H_2-air flame mechanism reduction
PCAS and PCAF provided identical reduced mechanisms



I. Gy. Zsély, T. Turányi: The influence of thermal coupling and diffusion on the importance of reactions: The case study of hydrogen-air combustion, *Phys.Chem.Chem.Phys.*, **5**, 3622-3631 (2003)

Reaction removal 4: PCAF with simulation error minimization (SEM-PCAF)

1. Generation of many reduced mechanisms

The simulation error does not change monotonically with the eigenvalue and eigenvector **thresholds** in the PCAF method.
Many reduced mechanisms are generated by **trying various thresholds.**

2. Making the reduced mechanisms to be living

Some of the obtained reduced mechanisms contain **non-living species,** whose important forming reactions are added based on **F**-matrix analysis.

3. Simulation of mechanisms and storing results

Simulations are carried out: **errors** and required **CPU times are recorded**

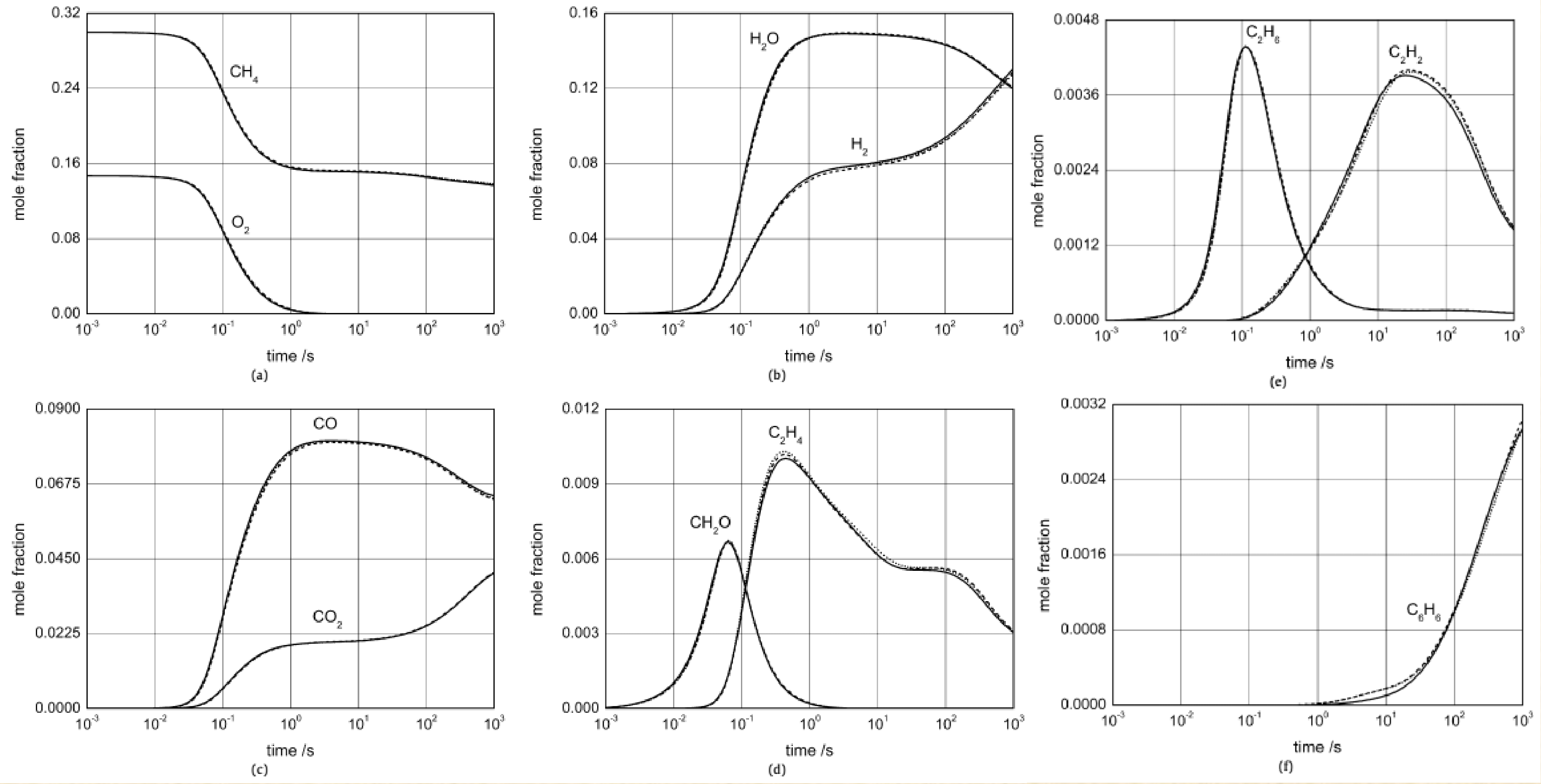
4. Finding the fastest reduced mechanism with small simulation error

Many different reduced mechanisms **have similarly small error**.

The reduced mechanism which can be simulated the fastest was selected from the accurate ones as the best one.

T. Nagy, T. Turányi: Reduction of very large reaction mechanisms using methods based on simulation error minimization, *Combust. Flame*, **156**, 417–428 (2009)

SEM case study 1: gas-phase chemistry in solid-oxide fuel cells (SOFC): partial oxidation of methane



——— original mechanism 6874 reactions of 345 species

- - - - - **SEM-CM** **613 reactions of 47 species** **58x speed up**

· · · · · · **SEM-CM+SEM-PCAF** **297 reactions of 47 species** **103x speed up**

Simulation time scales linearly with the number of reactions.

SEM case study 2: Reduction of the NUIG natural gas mech's for the ignition of CH_4/C_3H_8 mixtures at gas turbine conditions

system

- **NUIG NGM: 229 species**, 1359 reactions
- **22 scenarios** taken from RCM and Shock Tube experiments
- **CH_4: C_3H_8= 9:1**, **$\varphi(O_2)$=0.5-1.0,** diluent: Ar, N_2 38-75%
- **p=7-40atm, T=877-1465K**

Target ⇒ definition of simulation error:

$$\delta_{\tau\ \mathrm{MAX}} = \max_{\mathrm{i:scenarios}} \delta_{\tau\ \mathrm{i}}$$

- max. **5% error in ignition delay times** in adiabatic-isochoric simulations

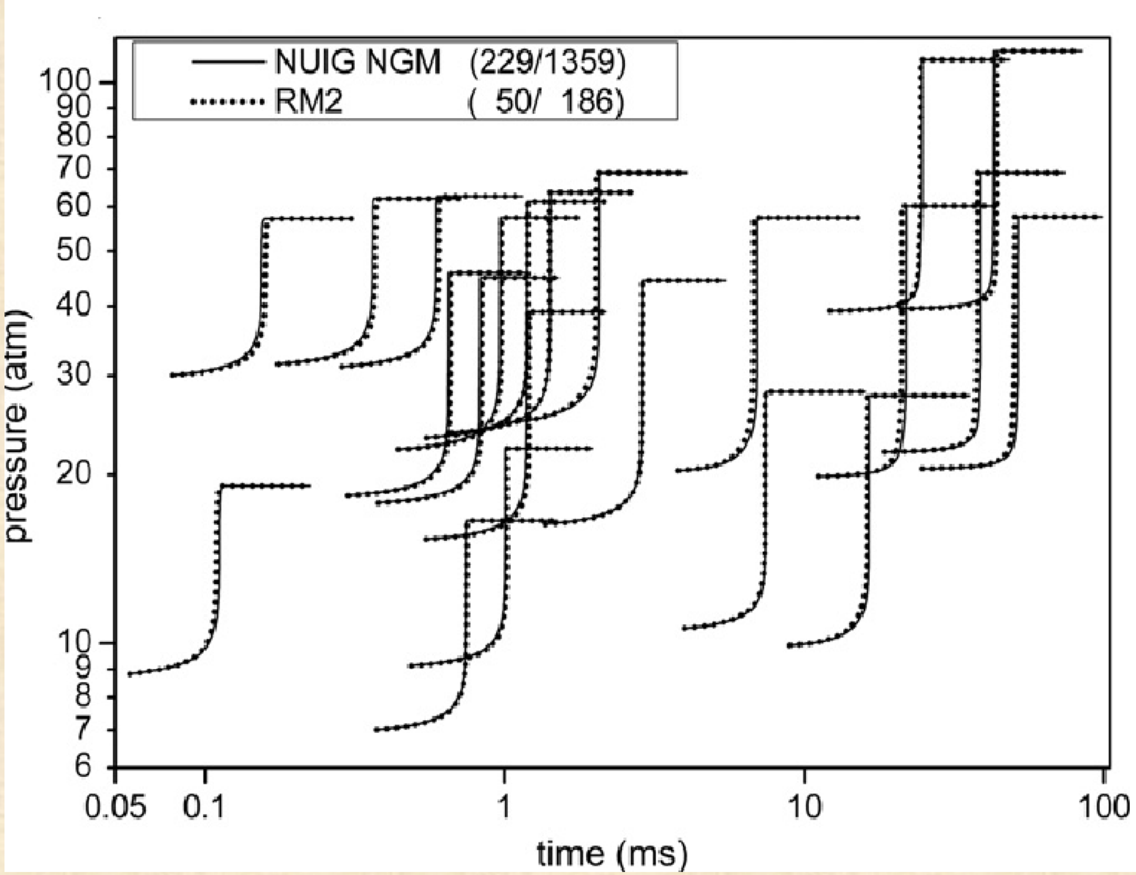
SEM-CM failed to reduce error for 22 scenarios in a single run.

Hierarchical reduction strategy

- **separate reduced mechanism is made for each scenario (22)**
- 22 scenarios are grouped into **6 regimes** based on similarity
- **intersection of species list** was made **for each regime**
- starting from them a **reduced mechanism is made for each regime (6)**
- starting **from their unified list a global reduced mechanism is made**

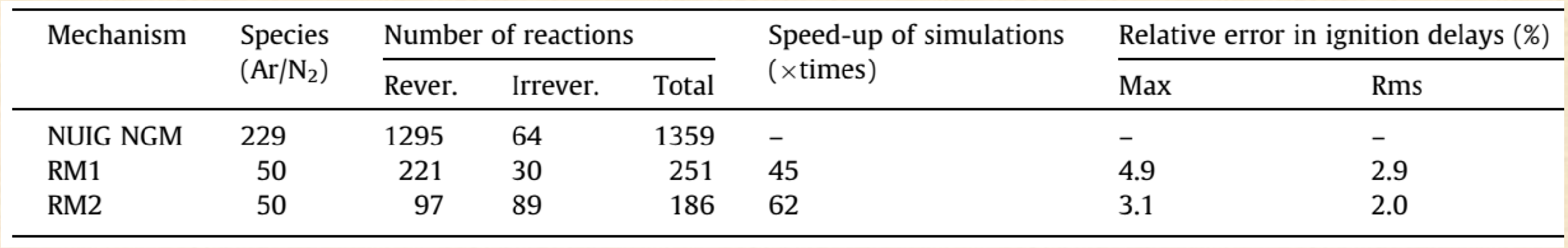
I. G. Zsély, T. Nagy, J.M. Simmie, H.J. Curran : Reduction of a detailed kinetic model for the ignition of methane/propane mixtures at gas turbine conditions using simulation error minimization methods, *Combust. Flame*, **158**, 1469–1479 (2011)

SEM case study 2: Reduction of the NUIG natural gas mech's for the ignition of CH_4/C_3H_8 mixtures at gas turbine conditions



RM1
Mechanism after species removal with SEM-CM

RM2
Mechanism after reaction removal with SEM-PCAF



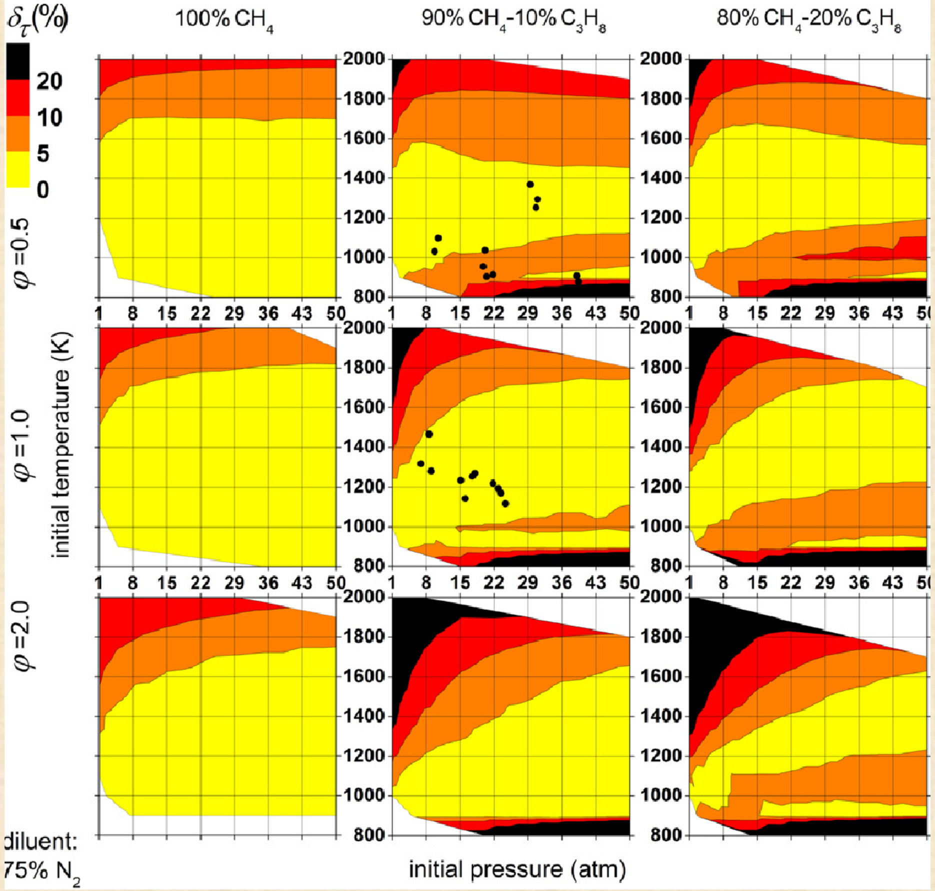
Mechanism	Species (Ar/N_2)	Number of reactions			Speed-up of simulations (×times)	Relative error in ignition delays (%)	
		Rever.	Irrever.	Total		Max	Rms
NUIG NGM	229	1295	64	1359	–	–	–
RM1	50	221	30	251	45	4.9	2.9
RM2	50	97	89	186	62	3.1	2.0

SEM case study 2: Reduction of the NUIG natural gas mech's for the ignition of CH_4/C_3H_8 mixtures at gas turbine conditions

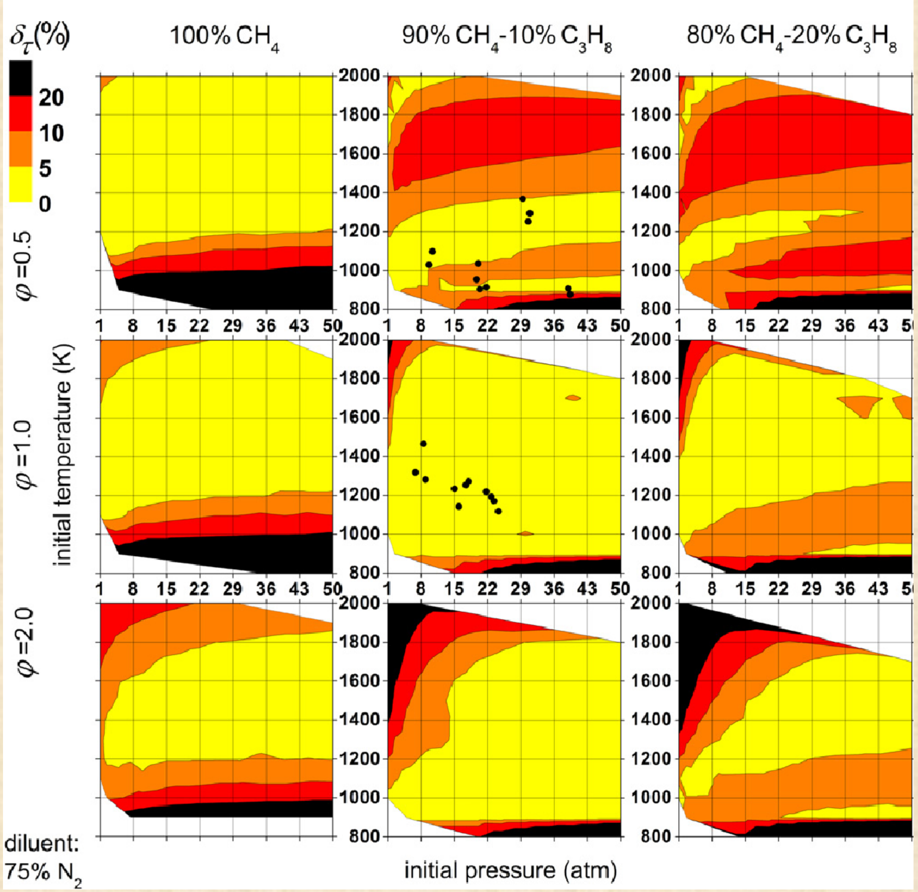
Robustness analysis

At what range of conditions can the reduced mechanism reproduce the simulation result of the original mechanism ?

RM1



RM2



Accurate in a much wider range. Reaction removal reduces robustness.

SEM case study 3: Reduction of the NUIG natural gas mech's for the ignition of $CH_4/C_2H_6/C_3H_8$ mixtures at gas turbine conditions

- **NUIG NGM**: 228 species/1359 reactions
- **Target**: reproduction of **temperature profiles during ignition** for **40,243 relevant conditions** (out of 138,240) **[project funded by ROLLS ROYCE]**
- **Matrix of conditions:**

Problem:
SEM cannot be run for such a large number of conditions!

Solution:
In an iterative procedure.
25 worst-case scenarios were identified and the final reduction was done for these.

param.	**investigated values**															
Fuel:	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
CH_4	10	9	9	8	8	8	7	7	7	7	6	6	6	5	5	4
C_2H_6	0	1	0	2	1	0	3	2	1	0	3	2	1	3	2	3
C_3H_8	0	0	1	0	1	2	0	1	2	3	1	2	3	2	3	3

#	**1**	**2**	**3**	**4**
N_2 vol%	0	10	20	30

#	**1**	**2**	**3**
φ_{air}	0.5	1.0	2.0

#	**1**	**2**	**3**	**4**
m_{H2O}/m_{air}	0.0	0.1	0.2	0.3

#	**1**	**2**	**3**	**4**	**5**	**6**
p_{ini}/atm	1	5	15	25	35	45

#	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
T_{ini}/100K	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20

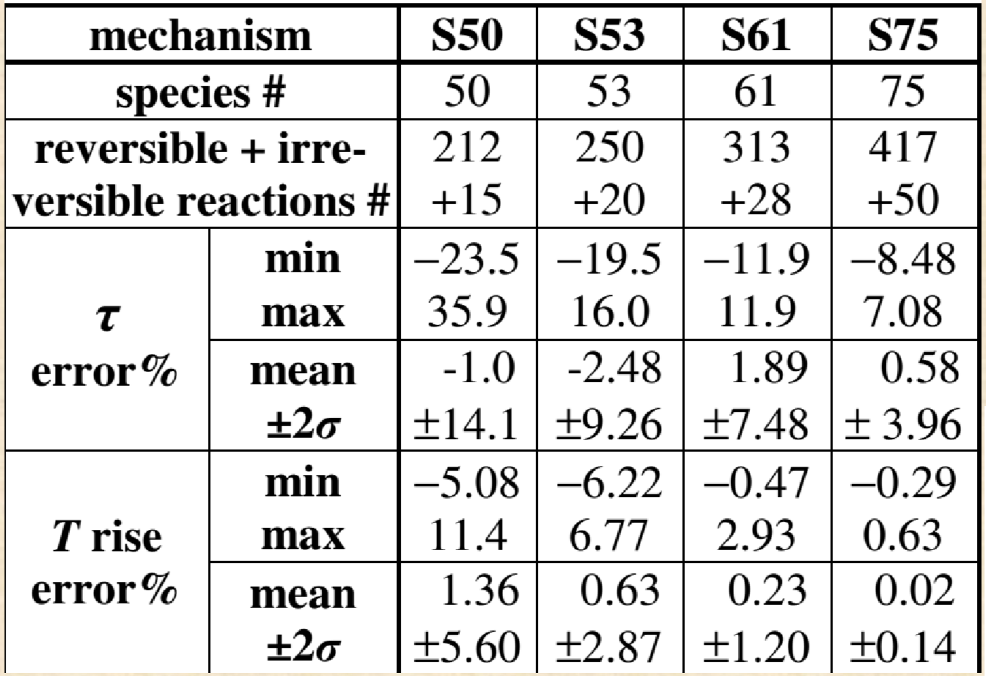
constraint	constant volume	constant pressure

T. Nagy, I. G. Zsély, H.J. Curran : Reduction of a detailed kinetic model for the ignition of methane/ethane/propane mixtures at gas turbine conditions using simulation error minimization methods, *Proceedings of the European Combustion Meeting* (2011)

SEM case study 3: Reduction of the NUIG natural gas mech's for the ignition of $CH_4/C_2H_6/C_3H_8$ mixtures at gas turbine conditions

Identifying low-number of representative ("worst-case") scenarios:

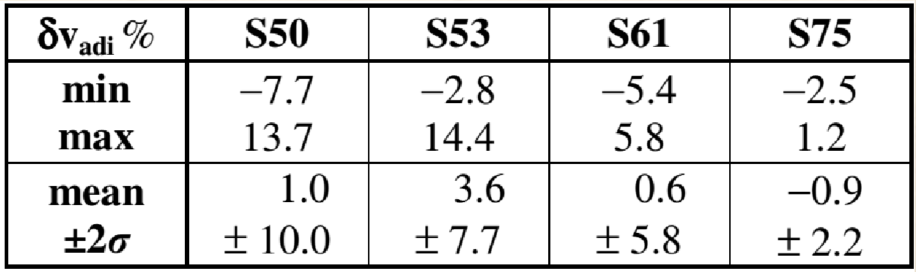
1. Accurate **reduced mechanism** was made for **three extreme scenarios**.
2. The reduced mechanism **was tested on all 40,243** scenarios.
3. A **scenario with the largest error** was selected.
4. Accurate **reduced mechanism** was made **for all selected** the scenarios.
5. **Steps** 2-4 were **repeated** until the mechanism became **globally accurate**.



mechanism		S50	S53	S61	S75
species #		50	53	61	75
reversible + irreversible reactions #		212 +15	250 +20	313 +28	417 +50
τ error%	min max	−23.5 35.9	−19.5 16.0	−11.9 11.9	−8.48 7.08
	mean $\pm 2\sigma$	-1.0 ±14.1	-2.48 ±9.26	1.89 ±7.48	0.58 ± 3.96
T rise error%	min max	−5.08 11.4	−6.22 6.77	−0.47 2.93	−0.29 0.63
	mean $\pm 2\sigma$	1.36 ±5.60	0.63 ±2.87	0.23 ±1.20	0.02 ±0.14

Error in 40,243 ignition scenarios.

- **25 scenarios were identified**
- **4 reduced mechanisms with species removal**
- **Tested in 40,243 scenarios and in 58 flame simulations.**



δv_{adi} %	S50	S53	S61	S75
min max	−7.7 13.7	−2.8 14.4	−5.4 5.8	−2.5 1.2
mean $\pm 2\sigma$	1.0 ± 10.0	3.6 ± 7.7	0.6 ± 5.8	−0.9 ± 2.2

Error in 58 1D flame scenarios.

τ error %: rel. error of ign. delay time, δv_{adi}%: rel. error of adia. flame speed

Summary

1. **In all current methods** for skeletal reduction **the controlling parameter** of the method **is not directly related to the error of reduction.**

2. **New reduction philosophy: SIMULATION ERROR MINIMIZATION**
   - **Thousands of candidate** reduced **mechanisms are generated** in a guided way.
   - **The best** (smallest, fastest) mechanism **is accepted**.
   - **Simulation error of the target property drives the reduction.**

3. **SEM-CM: guided building up of a series of consistent reduced mechanisms**.

4. **SEM-PCAF: optimized PCAF** method for the elimination of reactions

5. **SEM-CM** and **SEM-PCAF** **together are very effective** for the reduction of large reaction mechanisms

T. Nagy, T. Turányi, *Combust. Flame*, **156**, 417–428 (2009)

I. G. Zsély, T. Nagy, J.M. Simmie, H.J. Curran, *Combust. Flame*, **158**, 1469–1479 (2011)

T. Nagy, I. G. Zsély, H.J. Curran, *Proceedings of the European Combustion Meeting* (2011)