Aerospace Combustion

Lecture 7:

Short Introduction to Chemical Mechanism Reduction

Chemical Mechanisms

Current Status of Mechanism Development

1. Many simple mechanisms exist which are tuned for a small range of boundary conditions and molecules.
2. A mechanism developed for one class/range of phenomena may not be applicable to another class/range of phenomena
3. A mechanism is comprehensive only if it validated against experimental data of all relevant phenomena and parametric ranges
4. Validation is meaningful only if experimental data are accurate/meaningful
5. Presently, no comprehensive detailed mechanisms exist even for simple fuels

Chemical Mechanisms

Mechanism Construction

Species

- Reactants
- Intermediates, Radicals
- Products

Elementary Reactions

Physico-chemical Data for all Species

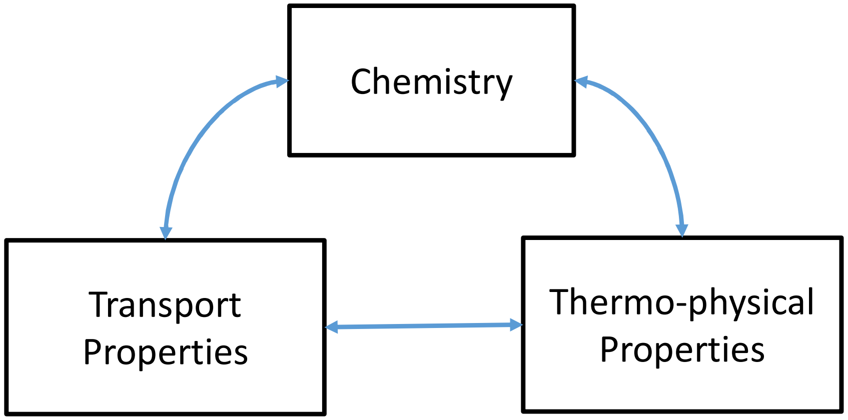
- Enthalpy of Formation
- Entropy
- Heat Capacity
- Transport Properties

Rate Constants of Reaction

- Phenomenological Arrhenius law

$$k = A \cdot e^{\left(-E_a/RT\right)}; \quad k = A \cdot T^n e^{\left(-E/RT\right)}$$

- Pressure Dependency



Transport Properties

- Viscosity
- Diffusion
- Thermal Conductivity
- Thermal Diffusion
- Speed of Sound

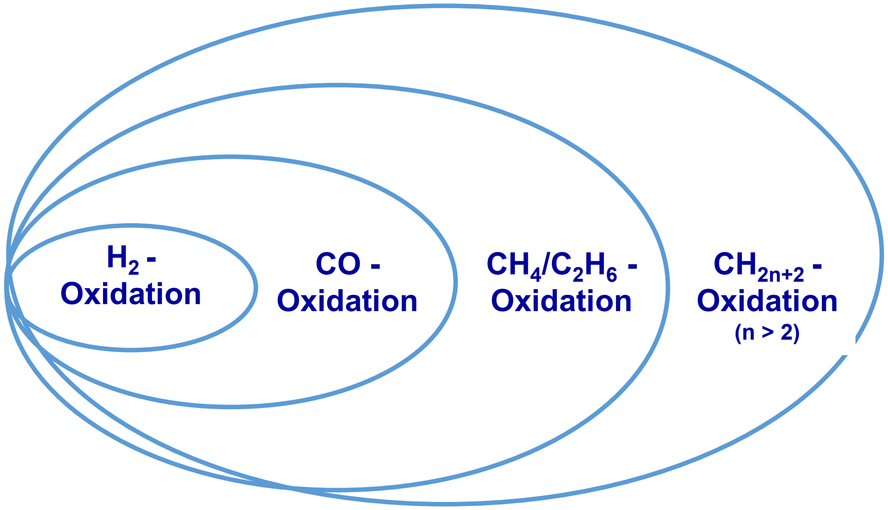
Thermo-chemical Properties

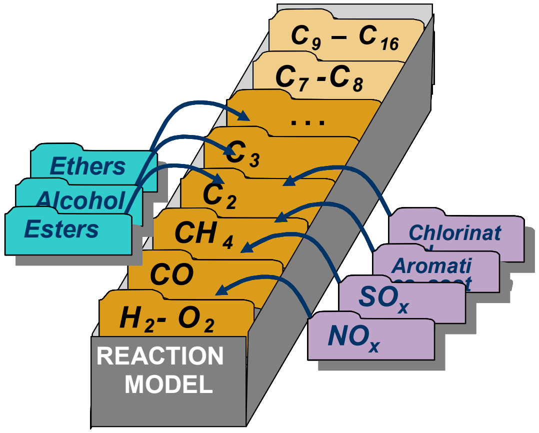
- Enthalpy, Entropy of formation
- Constant pressure and constant volume heat capacities
- Compressibility
- Thermal Expansion

Chemical Mechanisms

Hierarchical Mechanism Structure

- Chemical behavior of small species is almost independent of surrounding species since it is a function of its chemical interaction potential
- This holds as well for the transport properties





Molecule	H_2	CH_4	C_3H_8	C_6H_{14}	$C_{16}H_{34}$
	Hydrogen	Methane	Propane	Hexane	Cetane
Species	9	30	100	450	1200
Reactions	34	200	400	1500	7000

Chemical Mechanisms

Reduced Chemical Kinetic Schemes

Detailed schemes are often far too large to be included in 3D-unsteady CFD tools. Hence, reduced schemes are required which are small enough to be included in CFD tools (< 15 species, < 20 reactions) but sufficiently accurate to produce reasonable results.

Different methods to handle this problem

- Flamelet library based models
    - Adiabatic flamelet
    - Non-adiabatic flamelets
    - Flamelet Generated Manifolds (FGM)

(quite often they use detailed kinetic model but assume chemical equilibrium)

- Finite rate chemistry models
    - Chemical based reduction
        - Physico-chemical
        - Flame structure
    - Mathematical based reduction
        - Intrinsic low dimensional manifold (ILDM)
        - Quasi-steady state analysis (QSSA)
        - Computational singular perturbation (CSP)
        - Sensitivity analyses (SA)

(reduced kinetic schemes essential)

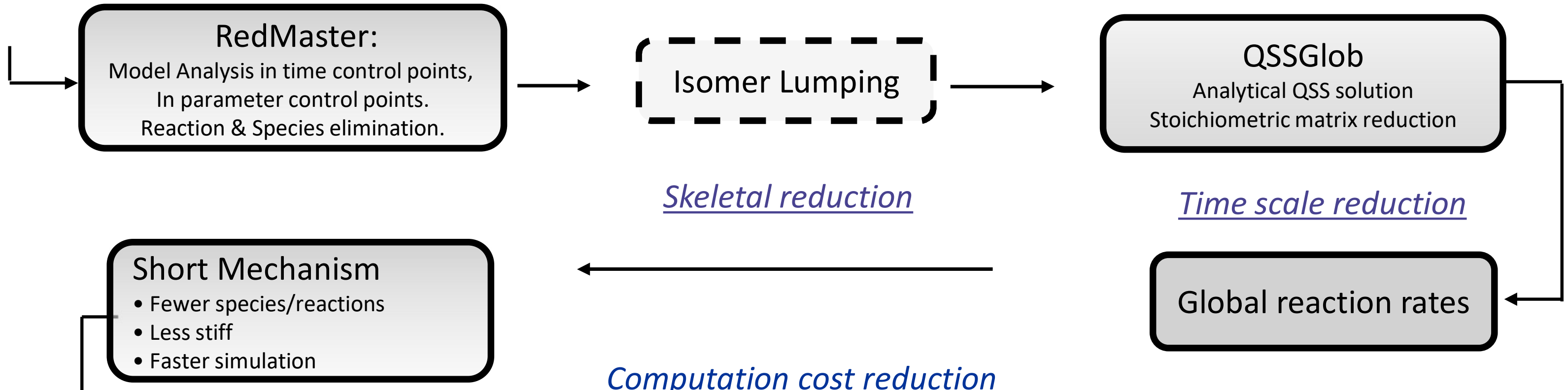
Mechanism Reduction

Strategy and Tools for Mechanism Analysis and Reduction

Detailed mechanisms
CH_4: 62 Species
$nC_{10}H_{22}$: 179 Species

Skeletal mechanisms
CH_4: 28 species
$nC_{10}H_{22}$: 118 species

Reduced mechanisms
CH_4: 16 species
$nC_{10}H_{22}$: 40 species



RedMaster:
Model Analysis in time control points,
In parameter control points.
Reaction & Species elimination.

Isomer Lumping

QSSGlob
Analytical QSS solution
Stoichiometric matrix reduction

Skeletal reduction

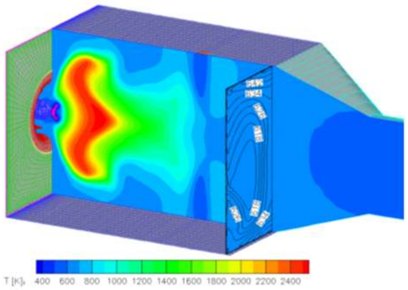
Time scale reduction

Global reaction rates

Short Mechanism
- Fewer species/reactions
- Less stiff
- Faster simulation

Computation cost reduction

CFD simulations



Time savings: factors of 10 ~ 100

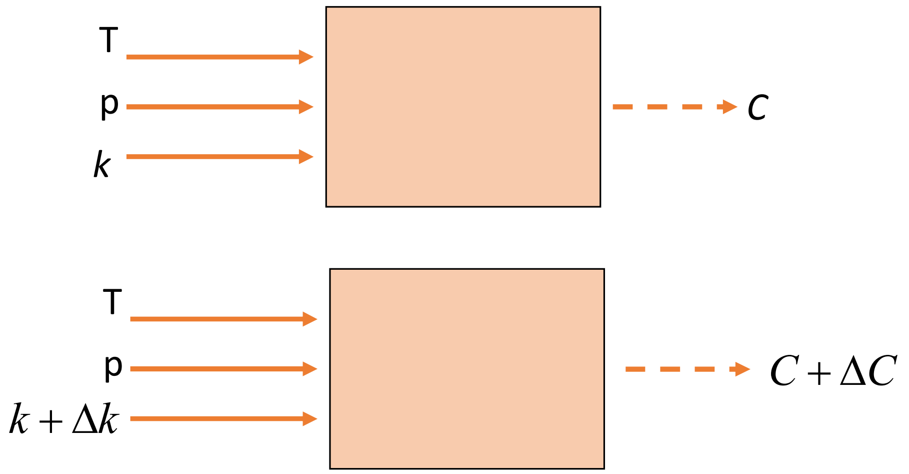
Mechanism Reduction

Mechanism Analysis

Local Sensitivity Coefficient

Determination of the sensitivity of a solution to a perturbation in vector *C* with θ_j any perturbation and the result Ψ_i of the system to the perturbation:

$$\theta_j$$



$$\Psi_i$$

$$S=\frac{\Delta C}{\Delta k} \Rightarrow s_{ji}=\frac{\partial c_j}{\partial \theta_i}$$

Sensitivity coefficient

Mechanism Reduction

Mechanism Analysis

Local Normalized Sensitivity Coefficient

$$S_j = \frac{\theta_j}{\Psi_i}\frac{\partial \Psi_i}{\partial \theta_j} = \frac{\partial \ln \Psi_i}{\partial \ln \theta_j}$$

Overall normalized sensitivity coefficient B_i is the sum of all local sensitivity coefficient

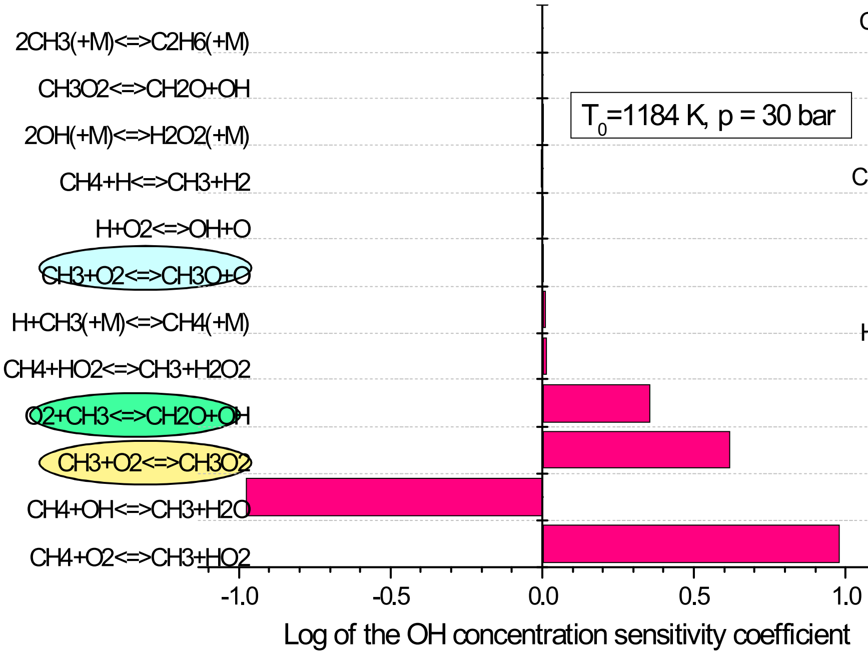
$\boldsymbol{B_i}$ is a measure of the effect of changing parameter $\boldsymbol{\Phi_i}$ on the group of perturbed outputs

$$B_i = \sum_j^p \left(\frac{\partial\ ln\ \Psi_j}{\partial\ ln\ \theta_i} \right)^2$$

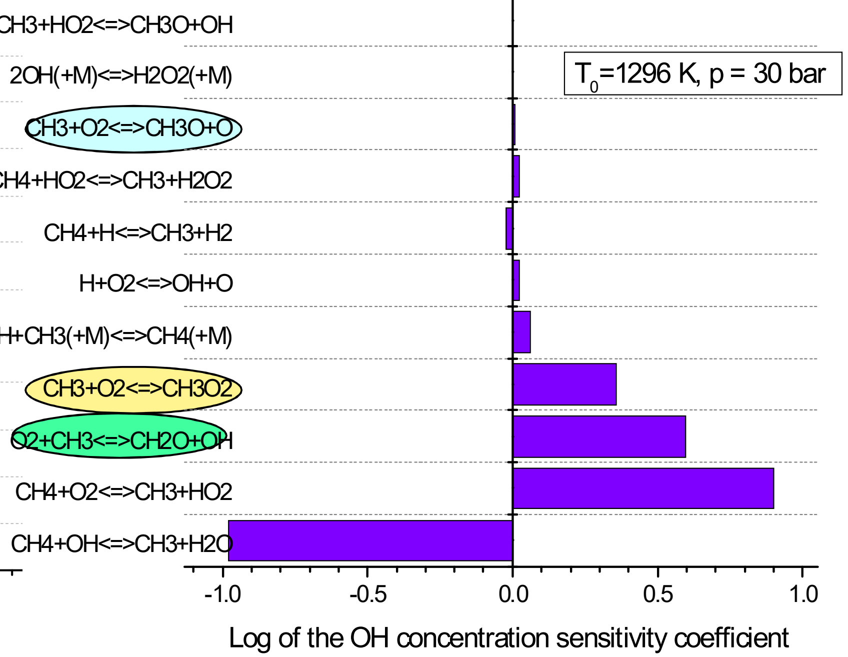
Mechanism Reduction

Sensitivity of Ignition delay (OH concentration) to reaction rates

CH3+O2 → CH3O2



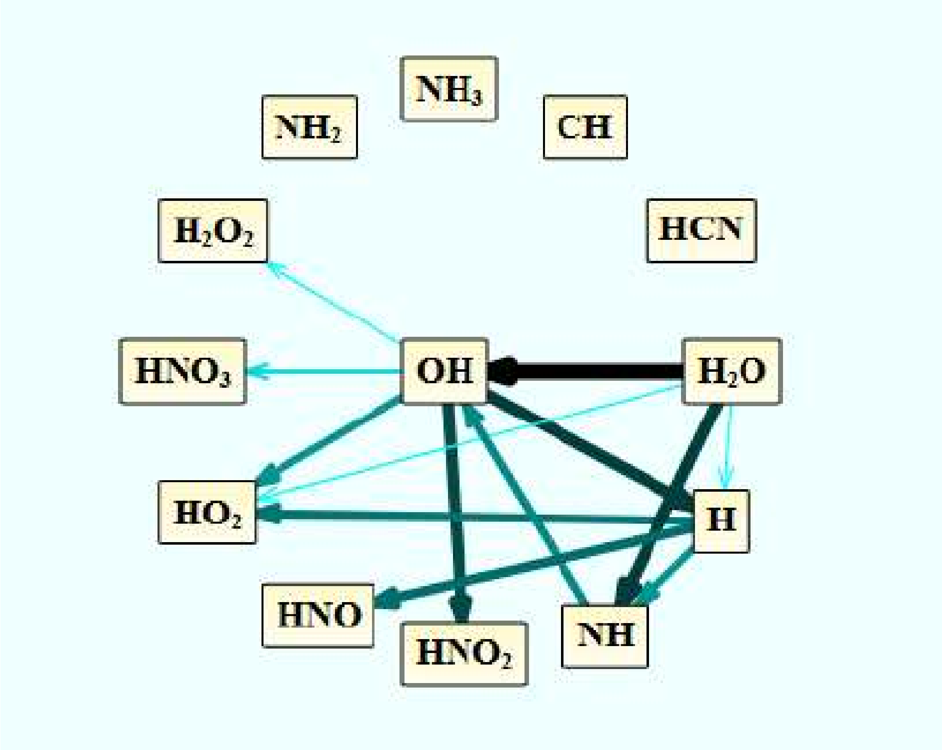
CH3+O2 → CH2O+OH



Two concurrent cannels:	CH3+O2 → CH2O+OH	(for T > 1200 K)
	CH3+O2 → CH3O2 → ...CH2O+OH	(for T < 1200 K)

Mechanism Reduction

Rate of Production Analysis



A calculation of reaction contributions to the production rates of species:

The reaction ***i*** can be considered as unimportant if the rate of production R_{ij}, of species ***j*** in reaction ***i***, is less than a chosen δ for all times in comparison to the maximum of the corresponding rates in all other occurring reactions

$$\Delta R_{ij} = \int_0^{\tau} W_{ij} dt < \delta \qquad W_{ij} = \frac{\nu_{ij} w_i}{\nu_{\max,j} w_{\max}}$$

Mechanism Reduction

Flow of Atoms Analysis

Discrimination of reactions or species on the base of calculation of the flux of atom *A* from species to species in each reaction step.

Atom flux $$A_{ijk} = (w_i \, n_{A,j} \, n_{A,k}) / N_{A,i}$$

$n_{A,j}$ is the number of atoms *A* in *j*, $n_{A,k}$ is the number of *A* in *k*, and $N_{A,i}$ is the total number of *A* in the reaction *i*.

$$\xi_{A,k} = \left| \left(\left| F^{+}_{A,k} \right| - \left| F^{-}_{A,k} \right| \right) / F^{tot}_{A} \right|$$

$$F^{+}_{A,k} = \sum_{i,j} \{ A_{ijk} > 0 \} \qquad F^{-}_{A,k} = \sum_{i,j} \{ A_{ijk} < 0 \}$$

F^{tot}_{A} the total atomic flux for a given flow chart

F^{+} F^{-} the fluxes for formation and consumption of *A*.

A species may be neglected when it is almost stationary $\xi \rightarrow 0$ and also when its net atomic fluxes A are small compared to F^{tot}_{A}.

Mechanism Reduction

Determination of Important Reactions

The overall sensitivity type measure for identification of important reactions:

$$A_i = \sum_{j}^{K} \left(\frac{\partial \ln R_j}{\partial \ln k_i} \right)^2$$

R_j - the rate of production of species *j,*
k_i - coefficient of reaction rate *i,*
K - is a number of species in a model.

A reaction *i* is considered important if its coefficients ***A_i***, calculated as sum for all species are bigger then a chosen threshold

$$A_i \geq \Delta$$

Mechanism Reduction

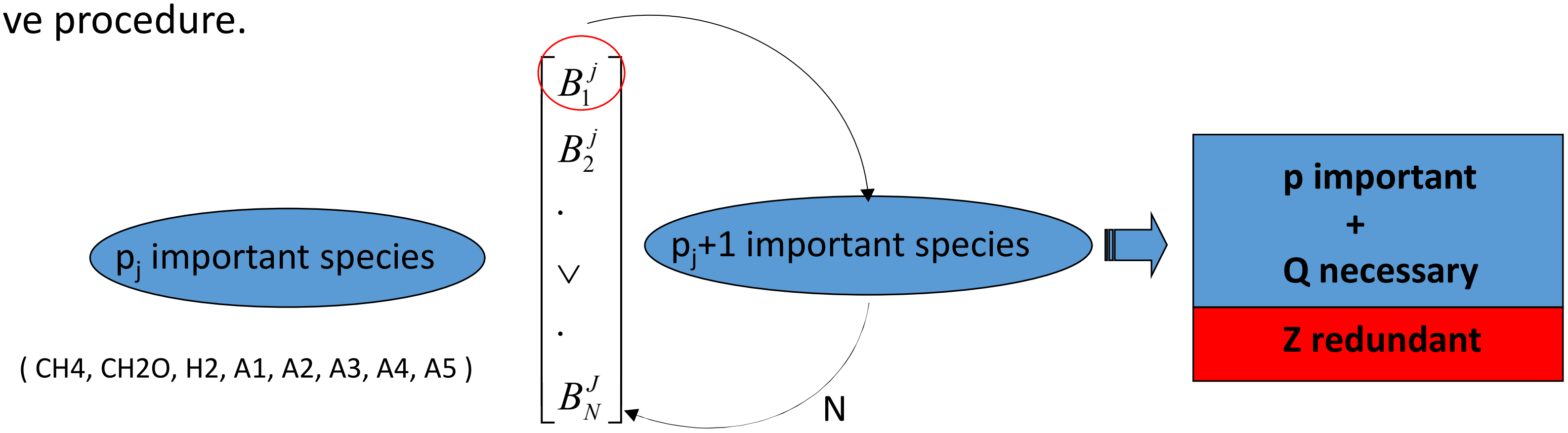
Determination of Important Species

The overall normalized sensitivity coefficient:

$$B_j = \sum_i^p \left(\frac{\partial \ln R_i}{\partial \ln c_j} \right)^2$$

R_i - the rate of production of species *i*,
c_j - concentration of species *j*,
p – the number of important species given by the investigator.

B_j yields the effect of a change of the concentration of species c_j on the rate of production of species *i*, R_i, from group of *p* important species.
The group of necessary species, which are most coupled with important species has to be identified by an iterative procedure.

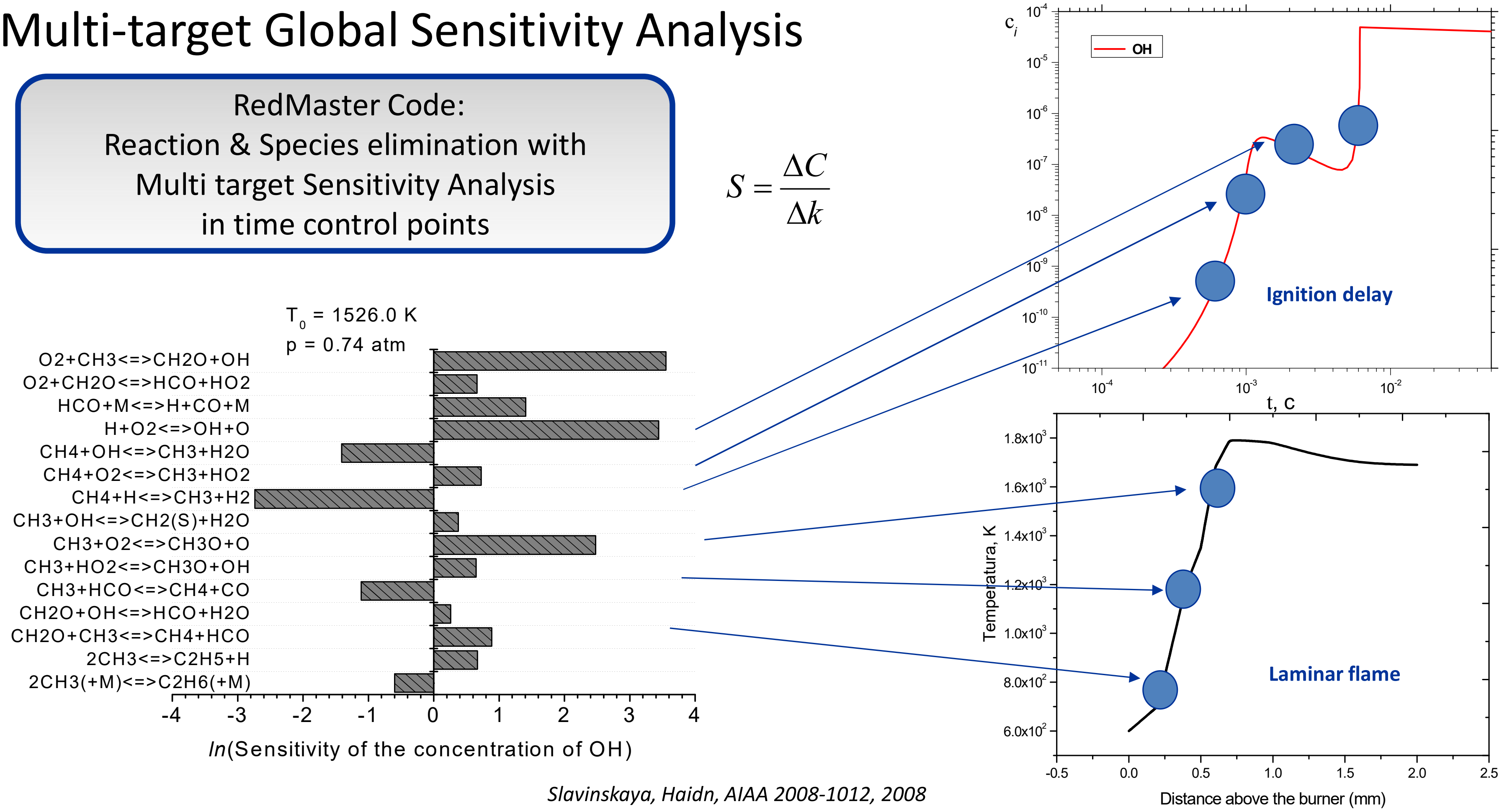


Mechanism Reduction

Multi-target Global Sensitivity Analysis

RedMaster Code:
Reaction & Species elimination with
Multi target Sensitivity Analysis
in time control points

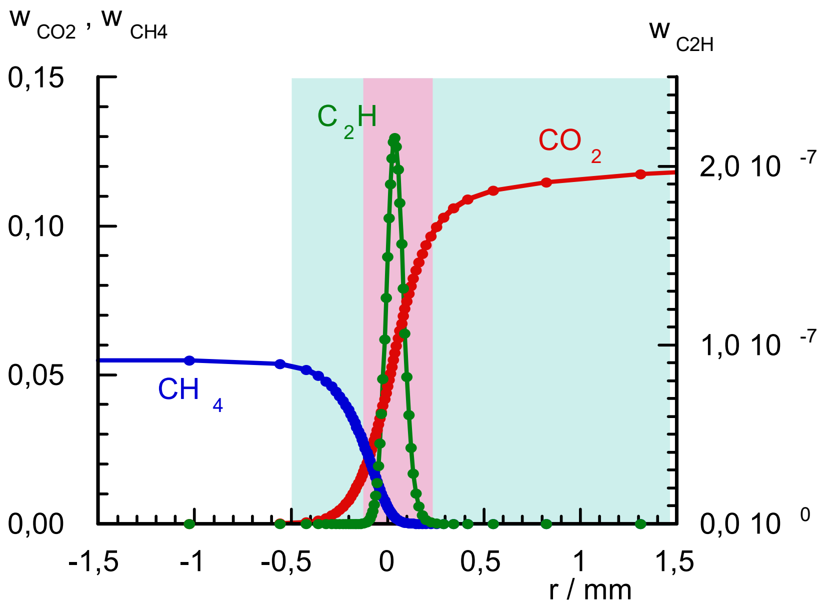
$$S = \frac{\Delta C}{\Delta k}$$



Slavinskaya, Haidn, AIAA 2008-1012, 2008

Mechanism Reduction

Time Scale Methods: QSS Approach



1-dimensional cut through a CH_4-air flame

Problems:

- extremely high dimensionality of the system!
- non-linear chemical source terms
- stiffness of the governing equation system
- different chemical time scales do not only introduce stiffness, but also cause the existence of very small length scales

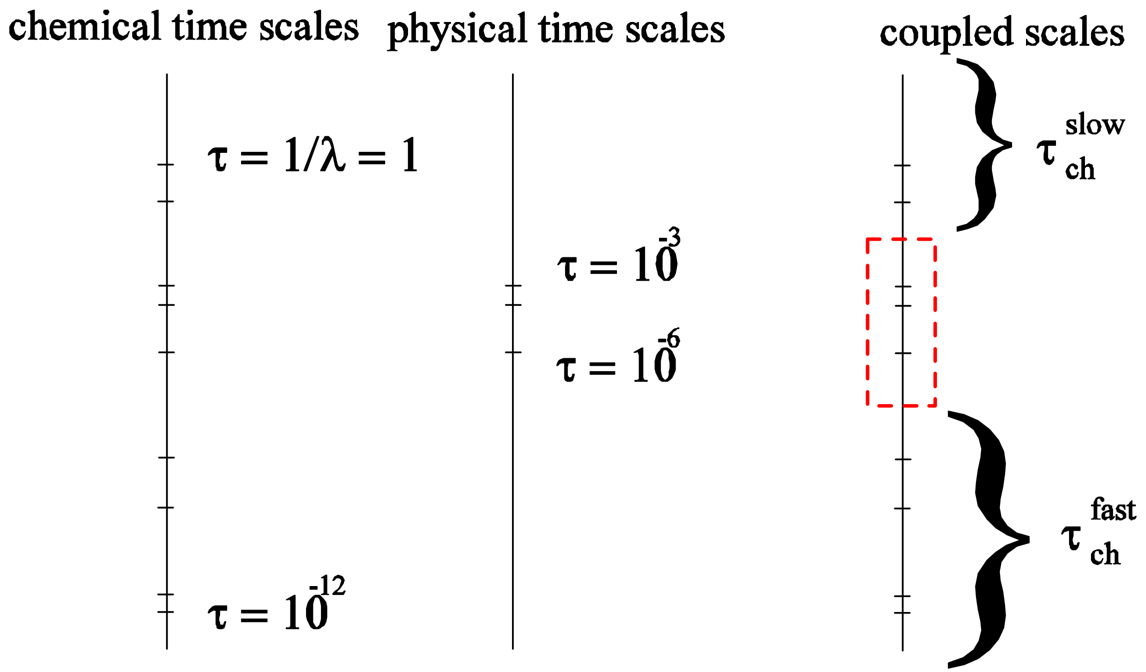
- Is it possible to decouple the fast chemical processes?

- This would
  - reduce the number of governing equations
  - remove part of the scaling problems in space!

Mechanism Reduction

Multi – Scales and Hierarchy of Processes

$$\frac{d\psi}{dt} = F(\psi)$$

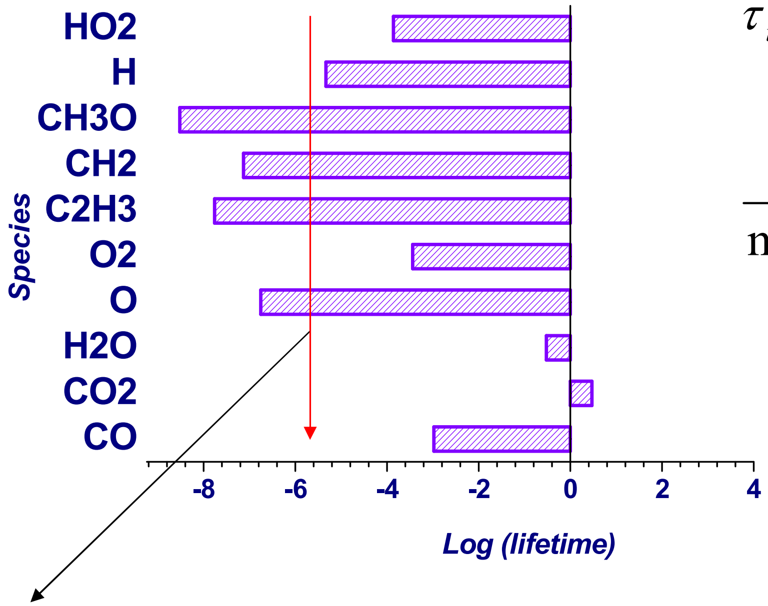


Chemical kinetic ODEs are multi-scale models: processes with different time scales – STIFF ODEs

Mechanism Reduction

Time Scale Methods: QSS Species

- the rate at which species ***i*** is consumed is much faster than the rate by which it is produced
- the concentrations and lifetime of QSS species are very small



$$\tau_i^c = -1\Big/\frac{\partial \omega_i}{\partial c_i} = \left|1/J_{ii}\right|$$

$$\frac{\left|R_j^p - R_j^c\right|}{\max\left(\left|R_j^p\right|,\left|R_j^c\right|\right)} << \delta$$

$$\frac{dC_{QSS_j}}{dt} = 0$$

<u>QSS species:</u> CH3O, O, CH2, C2H3

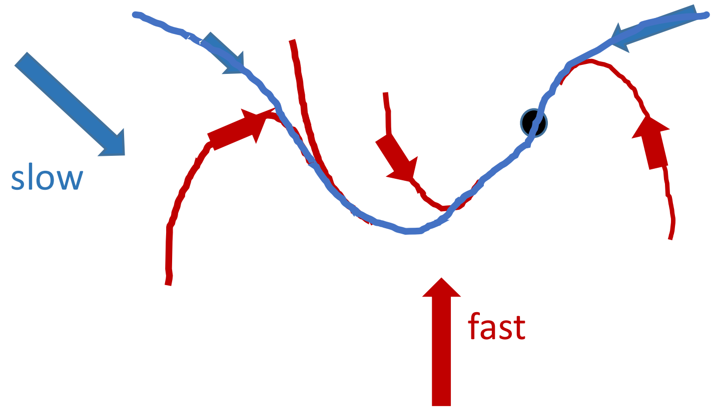
Searching for the Quasi-Steady-State (QSS) species (mostly intermediate radicals) to obtain more simple system of kinetic equations .

Mechanism Reduction

Intrinsic Low Dimensional Manifold

Slow chemical processes solved with the flow

- Decouple fast and slow chemical processes.
- Reduce number of equations
- Fast time scales are determined from slow ones



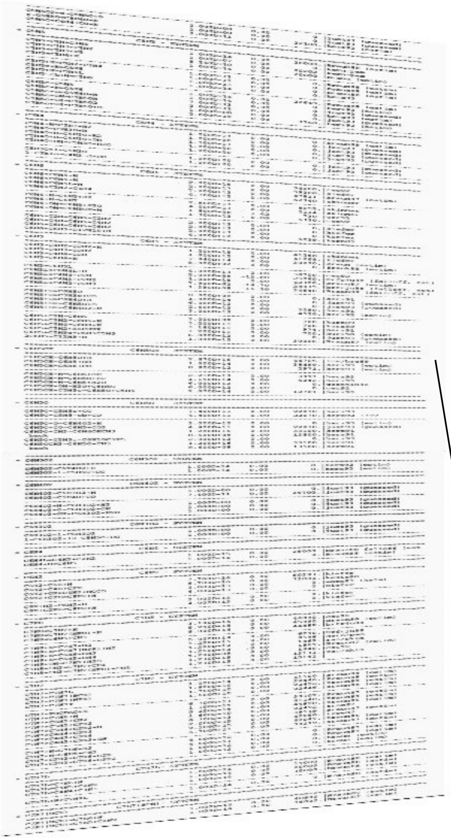
Identify Intrinsic Low-Dimensional Manifolds (ILDM).

- Reduce kinetics to the manifolds.
- Project governing equations onto the manifold.

Mechanism Reduction

Reduction of Reaction Mechanisms

Detailed reaction mechanism



Skeletal reaction mechanism reduction factor 2-5)

1) $O + H_2 \rightarrow H + OH$
2) $H+ OH \rightarrow O + H_2$
3) $O + HO_2 \rightarrow OH + O_2$
4) $H + O_2 + M \rightarrow HO_2 + M$
5) $H + O \rightarrow O + OH$
6) $O + OH \rightarrow H + O_2$
7) $H + OH + M \rightarrow H_2O + M$
8) $H + HO_2 \rightarrow O + H_2O$
9) $H + HO_2 \rightarrow O_2 + H_2$
10) $OH + H_2 \rightarrow H + H_2O$
11) $2OH \rightarrow O + H_2O$
12) $OH + CO \rightarrow H + CO$
13) $O + H_2O \rightarrow 2OH$
14) $H + CO \rightarrow OH + CO$
15) $H + HO_2 \rightarrow 2OH$
16) $HCO + M \rightarrow H + CO + M$
17) $H + CO + M \rightarrow HCO + M$
18) $H + HCO \rightarrow H2 + CO$
19) $HCO + O \rightarrow HO2 + CO$

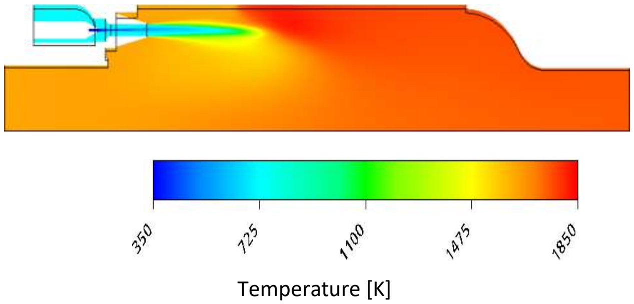
RedMaster Code:
Multi target analysis and
Reduction with keeping
of predictive capabilities

QSSGlob Code
Analytical QSS solution
Stoichiometric matrix reduction

Global reduced mechanism (reduction factor 2 - 3)

(1) $2\ H_2 + O_2 \rightarrow 2\ H_2O$
(2) $CO + O_2 + H_2 \rightarrow CO_2 + H_2O$

Numerical simulation



Mechanism Reduction

Reduced Mechanism Validation

Validation has to happen already during development

In order to be highly predictive it is mandatory to

- Use the largest possible data base with parameter variations of
    - Pressure
    - Initial temperature
    - Mixture ratio
    - Diluent concentrations

and is also recommended to take data from a sufficient large number of different experimental setups using as well different measurement techniques.

However, never forget to check the published data about uncertainty to avoid being led astray (i.e. old data from rapid compression engines can be biased due to induced convection, shock tubes should have a sufficient large diameter to educe boundary layer effects, ….)

Mechanism Reduction

Final Mechanism Validation Ignition Delay

Ignition delay times at low pressure are important for modeling the engine ignition and startup process but as well at higher pressures and different mixture ratios.

Furthermore, laminar flame speed is of key importance since it can be measured rather easily and it is defined by the heat release, i.e., the progress of the chemical reactions. Again, it is important to validate against for low pressure and high pressure data at various mixture ratios.

There are reactions which react differently depending on pressure (intermolecular collisions are responsible for this behavior).

What you should remember

- Explosive limits of H2/O2 mixtures
- General reaction mechanism (initiation, propagation and termination)
- Difference between light hydrocarbon (methane) and heavy hydrocarbon reactions
- NTC region for higher alkane combustion and its explanation
- Methods to generate reduced chemical kinetic schemes
- Development and validation procedures of such schemes

Annex: Chemical Kinetics

Mechanism for Ammonium-perchlorate Decomposition

			Arrhenius parameters		
			A	b	Ea
1)	$HClO_4$	$\rightleftharpoons ClO_3^* + OH^*$	1.0 e14	0.0	39100
2)	$HClO_4 + HNO$	$\rightleftharpoons ClO_3^* + H_2O + NO^*$	1.5 e13	0.0	6000
3)	ClO_3^*	$\rightleftharpoons ClO^* + O_2$	1.7 e13	0.5	0.0
4)	$Cl2 + O_2 + M$	$\rightleftharpoons ClO_2^* + Cl^* + M^*$	6.0 e08	0.0	1200
5)	$ClO^* + NO^*$	$\rightleftharpoons Cl^* + NO_2^*$	6.78 e12	0.0	311
6)	$ClO^* + ClOH$	$\rightleftharpoons Cl_2 + HO_2^*$	1.0 e11	0,0	10000
7)	$ClOH + OH^*$	$\rightleftharpoons ClO^* + H_2O$	1.8 e13	0.0	0
8)	$HCl + OH^*$	$\rightleftharpoons Cl^* + H_2O$	5.0 e11	0.0	750
9)	$Cl2 + H^*$	$\rightleftharpoons HCl + Cl^*$	8.4 e13	0.0	1150
10)	$ClO^* + NH_3$	$\rightleftharpoons ClOH + NH_2^*$	6.0 e11	0.5	6400
11)	$NH_3 + Cl^*$	$\rightleftharpoons NH_2^* + HCl$	4.5 e11	0.5	100
12)	$NH_3 + OH^*$	$\rightleftharpoons NH_2^* + H_2O$	5.0 e07	1.6	955
13)	$NH_2^* + O_2$	$\rightleftharpoons HNO + OH^*$	3.0 e09	0.0	0
14)	$NH_2^* + NO^*$	$\rightleftharpoons H_2O + N_2$	6.2 e15	-1.3	0
15)	$HNO + OH^*$	$\rightleftharpoons NO^* + H_2O$	1.3 e07	1.9	-950
16)	$HNO + O_2$	$\rightleftharpoons NO_2^* + OH^*$	1.5 e13	0.0	10000
17)	$HNO + H^*$	$\rightleftharpoons H_2 + NO^*$	4.5 e11	0.7	660
18)	$NO^* + H^* + M$	$\rightleftharpoons HNO + M$	8.9 e19	-1.3	740
19)	$HO^*_2 + N_2$	$\rightleftharpoons HNO + OH^*$	2.7 e10	0.5	41800
20)	$NO^* + HO_2^*$	$\rightleftharpoons NO_2^* + OH^*$	2.11 e12	0.0	480
21)	$H^* + NO^*_2$	$\rightleftharpoons NO^* + OH^*$	3.47 e14	0.0	1480
22)	$H_2 + OH^*$	$\rightleftharpoons H_2O + H^*$	2.16 e08	1.5	3430

$$k = A T^b e^{-Ea/T}$$

ANNEX Chemical Kinetics

Mechanism for Ammonium-perchlorate / HTPB Reactions

1) $Cl_2 + O_2 + M \rightleftharpoons ClO_2* + Cl* + M$
2) $ClO* + NO* \rightleftharpoons Cl* + NO*_2$
3) $HCl + OH* \rightleftharpoons Cl* + H_2O$
4) $Cl2 + H* \rightleftharpoons HCl + Cl*$
5) $NH_3 + Cl* \rightleftharpoons NH_2* + HCl$
6) $NH_3 + OH* \rightleftharpoons NH_2* + H_2O$
7) $NH_2* + O_2 \rightleftharpoons HNO + OH*$
8) $NH_2* + NO* \rightleftharpoons H_2O + N_2$
9) $HNO + OH* \rightleftharpoons NO* + H_2O$
10) $HNO + O_2 \rightleftharpoons NO_2* + OH*$
11) $HNO + H* \rightleftharpoons H_2 + NO*$
12) $NO* + H* + M \rightleftharpoons HNO + M$
13) $HO*_2 + N_2 \rightleftharpoons HNO + OH*$
14) $NO* + HO_2* \rightleftharpoons NO_2* + OH*$
15) $H* + NO*_2 \rightleftharpoons NO* + OH*$
16) $H_2 + OH* \rightleftharpoons H_2O + H*$
17) $CH_4 + Cl* \rightleftharpoons CH*_3 + HCl$
18) $CH_4 + H* \rightleftharpoons CH*_3 + H_2$
19) $CH_4 + OH* \rightleftharpoons CH*_3 + H_2O$
20) $CH*_3 + H* + M \rightleftharpoons CH_4 + M$
21) $CO + OH* \rightleftharpoons CO_2 + H*$
22) $CO + ClO* \rightleftharpoons CO_2 + Cl*$
23) $CO + ClO*_2 \rightleftharpoons CO_2 + ClO*$
24) $H* + O_2 \rightleftharpoons O* + OH*$
25) $CH_2* + H_2 \rightleftharpoons CH*_3 + H*$
26) $CH_2* + H* + M \rightleftharpoons CH*_3 + M$
27) $CH4 + O* \rightleftharpoons CH*_3 + OH*$
28) $OH+ + CH_3* \rightleftharpoons CH*_2 + H_2O$
29) $C_2H_4 + O2 \rightleftharpoons 2CO + 2H_2$
30) $Cl* + HO*_2 \rightleftharpoons ClO* + OH*$
31) $ClO* + O* \rightleftharpoons Cl* + O_2$
32) $H* + HCl \rightleftharpoons Cl* + H_2$
33) $HCl + O* \rightleftharpoons Cl* + OH*$
34) $Cl_2 + O* \rightleftharpoons Cl* + ClO*$
35) $N_2O + M \rightleftharpoons N_2 + O* + M$
36) $N_2O + OH* \rightleftharpoons N_2 + HO*_2$
37) $N_2O + O* \rightleftharpoons 2NO*$
38) $N_2O + O* \rightleftharpoons N_2 + O_2$
39) $N_2O + H* \rightleftharpoons N_2 + OH*$
40) $2H* + M \rightleftharpoons H_2 + M$
41) $2H* + H_2 \rightleftharpoons 2H_2$
42) $2H* + H_2O \rightleftharpoons H_2 + H_2O$
43) $2H* + CO_2 \rightleftharpoons H_2 + CO_2$
44) $ClO*_2 + NO* \rightleftharpoons ClO* + NO*_2$
45) $Cl* + ClO_2* \rightleftharpoons 2ClO*$
46) $ClO* + ClO* \rightleftharpoons Cl_2 + O_2$
47) $Cl* + HO*_2 \rightleftharpoons HCl + O_2$
48) $Cl* + O_2* + M \rightleftharpoons ClO*_2 + M$
49) $NO*_2 + O* \rightleftharpoons NO* + O_2$
50) $HNO + HNO \rightleftharpoons H_2O + N_2O$
51) $NO*_2 + NO*_2 \rightleftharpoons 2NO* + O_2$
52) $Cl* + N_2O \rightleftharpoons ClO* + N_2$
53) $2OH* \rightleftharpoons H_2O + O*$
54) $NH_2* + NO_2* \rightleftharpoons H_2O + N_2O$
55) $HNO + NH_2* \rightleftharpoons NH_3 + NO*$
56) $ClO* + HNO \rightleftharpoons HCl + NO*_2$
57) $HCl + HO_2 \rightleftharpoons ClO* + H_2O$
58) $NH_2* + NO* \rightleftharpoons H* + N_2 + OH*$
59) $NH_2* + NH_2* \rightleftharpoons NH* + NH_3$
60) $NH* + NO* \rightleftharpoons N_2 + OH*$
61) $NH* + NO* \rightleftharpoons H* + N_2 + O*$
62) $Cl* + NH_2* \rightleftharpoons HCl + NH*$
63) $ClO_2* + NH* \rightleftharpoons ClO* + HNO$
64) $N* + NO_2* \rightleftharpoons 2NO*$
65) $N* + N_2O \rightleftharpoons N_2 + NO$
66) $NH* + OH* \rightleftharpoons H_2O + N*$
67) $NH* + OH* \rightleftharpoons H_2 + NO*$
68) $NH* + NH_2 \rightleftharpoons N* + NH_3$
69) $HO_2* + CH_3* \rightleftharpoons O_2 + CH_4$
70) $CH_2 + CH_4 \rightleftharpoons 2CH_3*$