

Part of Prof. Keszei's „Modern reaction kinetics” course  
Topic 2

Time scale analysis and reduction of reaction mechanisms



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# Time scale analysis

## Lifetimes and time scales

### Half life:

Time period needed for the concentration of a species to decrease to  $1/2$ , if during this time it is not produced and the concentrations of all other species remains identical.

### Lifetime:

Time period needed for the concentration of a species to decrease to  $1/e$ , if during this time it is not produced and the concentrations of all other species remains identical.

Single first order reaction :  $Y = Y_0 e^{-kt}$

$A \rightarrow P$

$$\text{lifetime: } \tau = \frac{1}{k} \qquad \text{half life: } \tau_{1/2} = \frac{\ln 2}{k}$$

### Several first order reactions

(e.g. in photochemistry the reactions of an excited species):

$A \rightarrow P_1$

$\rightarrow P_2$

$\rightarrow P_3$

$$Y = Y_0 e^{-(k_1+k_2+k_3)t}$$

$$\text{lifetime: } \tau = \frac{1}{(k_1 + k_2 + k_3)}$$

## Lifetime

### Atmospheric chemistry:

small radical concentrations  $\Rightarrow$  radical-radical reactions are missing  
(e.g.  $2 \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ )  $\Rightarrow$  no  $Y_i^2$  type terms in the kinetic system of ODEs

$P_i$  effect of producing steps

$L_i$  effect of consuming steps

Production rate of  $Y_i$ :

$$dY_i/dt = P_i - L_i Y_i$$

$Y_i$  lifetime:

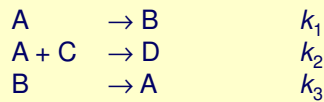
$$\tau = \frac{1}{L_i}$$

### General reaction mechanism:

$$Y_i \text{ lifetime: } \tau = -\frac{1}{j_{ii}} \quad \text{where } j_{ii} = \frac{\partial f_i}{\partial Y_i}$$

$j_{ii}$  is the  $i^{\text{th}}$  diagonal element of the Jacobian

### Example



Production rate of species A :

$$da/dt = -k_1 a - k_2 ac + k_3 b$$

$$da/dt = k_3 b - (k_1 + k_2 c) a$$

„Atmospheric chemical" lifetime:

$$dY_i/dt = P_i - L_i Y_i \quad \tau_A = 1/L_A = 1/(k_1 + k_2 c)$$

General lifetime:

$$j_{AA} = \frac{\partial (da/dt)}{\partial a} = -(k_1 + k_2 c) \quad \tau_A = -1/j_{AA} = 1/(k_1 + k_2 c)$$

### Slow variables and fast variables

The concentration of a single species is changed by  $\Delta y'_i$   
and the concentration change of the other species is negligible:

$$\Delta y'_i(t) = \Delta y'^0_i e^{j_{ii} t}$$

short lifetime species = the effect of perturbation decreases rapidly =  
the perturbed trajectory converges very fast to the the original trajectory  
⇒ **fast variable**

long lifetime species = the effect of perturbation does not decrease rapidly  
= the original and the perturbed trajectory are „parallel”  
⇒ **slow variable**

#### Consequences:

- fast variables „forget” their initial value
- the values of fast variables are determined by the values of the other variables
- the „slow/fast variable” classification is independent of the actual change of the variables in time ( $dY_i/dt$ )

### Eigenvector-eigenvalue decomposition of the Jacobian

$$\Lambda = \mathbf{W} \mathbf{J} \mathbf{V} \quad \mathbf{J} = \left\{ \frac{\partial f_i}{\partial Y_j} \right\}$$

$\Lambda$  diagonal matrix that contains the eigenvalues (complex eigenvalues!)

$\mathbf{W}$  matrix of left eigenvectors (row vectors)

$\mathbf{V}$  matrix of right eigenvectors (column vectors)

denote  $\mathbf{W}_f$  the matrix of left eigenvectors, related to small negative  $\text{Re}(\lambda)$   
(„eigenvectors related to fast directions”)

**Features:** the left and right eigenvectors are orthonormed:

$$\mathbf{I} = \mathbf{W} \mathbf{V}$$

$$\mathbf{I} = \mathbf{V} \mathbf{W}$$

$$\text{therefore: } \mathbf{J} = \mathbf{V} \Lambda \mathbf{W}$$

### Stiff systems 1

The eigenvalues define the time scales of a model:  $t_i = 1/|\text{Re}(\lambda_i)|$

Very different time scales  $\Rightarrow$  stiff mathematical models

Mathematicians' definition of stiffness:  
the ratio of the longest and shortest time scale

stiffness ratio  $S_1$

$$S_1 = \frac{1}{\min_i |\text{Re}(\lambda_i)|} \quad / \quad \frac{1}{\max_i |\text{Re}(\lambda_i)|}$$

longest time scale                      shortest time scale

$$S_1 = \max_i |\text{Re}(\lambda_i)| / \min_i |\text{Re}(\lambda_i)|$$

## Stiff systems 2

Physicists' and chemists' definition of stiffness:

the ratio of the characteristic („typical”) time scale and the shortest time scale

stiffness ratio  $S_2$

$$S_2 = \frac{\tau}{\frac{1}{\max_i |\operatorname{Re}(\lambda_i)|}}$$

characteristic time scale      shortest time scale

$$\text{stiffness ratio } S_2 = \tau \max_i |\operatorname{Re}(\lambda_i)|$$

$\tau$  is the characteristic time scale of the system

A model is considered stiff, if the stiffness ratio is large (e.g.  $10^8$ - $10^{12}$ )

The stiff systems of differential equations:

⇒ can be solved with special algorithms only

(„backward differentiation formulas”, „implicit solvers”)

⇒ stiffness changes with changing concentrations

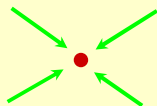
## Stability analysis of a stationary system

differential equation of the system       $d\mathbf{Y}/dt = \mathbf{f}(\mathbf{Y}, \mathbf{p})$

in the stationary point       $d\mathbf{Y}/dt = \mathbf{0}$

**Stable stationary point:**

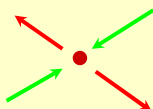
we move it out, goes back



Jacobian       $\mathbf{J} = \left\{ \frac{\partial f_i}{\partial y_j} \right\}$       the real parts of all eigenvalues are negative

**Unstable stationary point:**

we move it out, goes away

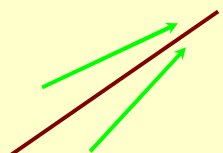


There exist at least one eigenvalue of the Jacobian having positive real part

## Stability analysis of a moving system

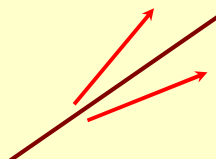
differential equation of the system  $d\mathbf{Y}/dt = \mathbf{f}(\mathbf{Y}, \mathbf{p})$

**Stable trajectory:** we move it out, goes back to the original trajectory



Jacobian  $\mathbf{J} = \left\{ \frac{\partial f_i}{\partial y_j} \right\}$  the real parts of all eigenvalues are negative

**Unstable trajectory:** we move it out, goes away



There exist at least one eigenvalue of the Jacobian that the real part of it is positive

**Chemical example:** autocatalytic runaway, explosions

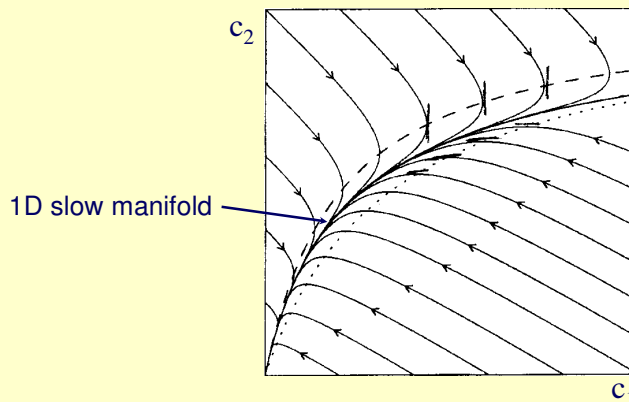
## Slow manifolds in dynamical systems

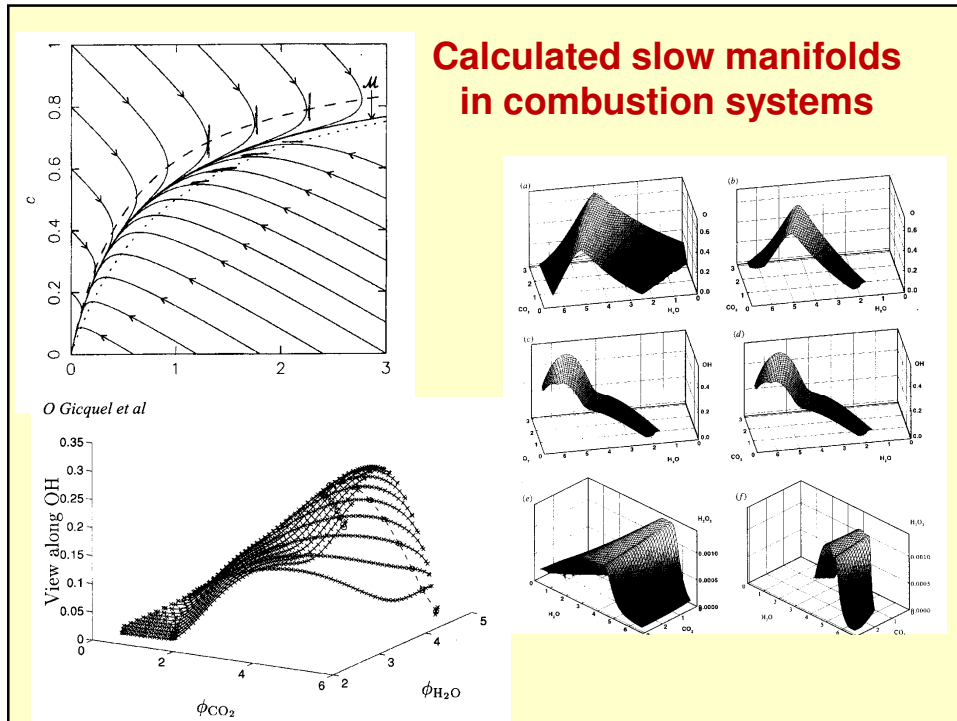
In the space of variables (in chemical kinetics: concentrations) the fast moving points approach a given object (called slow manifolds) and move slowly along it.

**2D manifold :** the trajectories approach a plane

**1D manifold:** the trajectories approach a (curved) line

**0D manifold:** the trajectories approach the equilibrium point





## Reduction of reaction mechanisms

## Advantages of mechanism reduction

### 1 Spatially homogeneous system

- described by an ordinary system of differential equations  
fast numerical simulation  
a few minutes simulation time of a model having several thousand species and several ten thousands of reactions
- nobody understands such a big mechanism.  
a skeleton model is needed to understand the chemistry

### 2 Spatially inhomogeneous system

- described by a partial system of differential equations  
very slow numerical simulation  
method of operator splitting is frequently used  
the chemistry and the advection/diffusion is simulated separately:

$$\frac{d\mathbf{c}(\mathbf{r},t)}{dt} = \mathbf{f}(\mathbf{r},t,\mathbf{c}) + \Theta(\mathbf{r},t,\mathbf{c},\nabla\mathbf{c},\nabla^2\mathbf{c})$$

Most of the computer time (e.g. 99%) is used for solving the chemical kinetic equations

Mechanism reduction offers a good possibility for speeding up the calculations!

## Redundant species in a mechanism

Important species and important features (like time to ignition)  
These should be simulated accurately

### Necessary species

These are also needed (should be present in a mechanism) for an accurate simulation of important species and important features

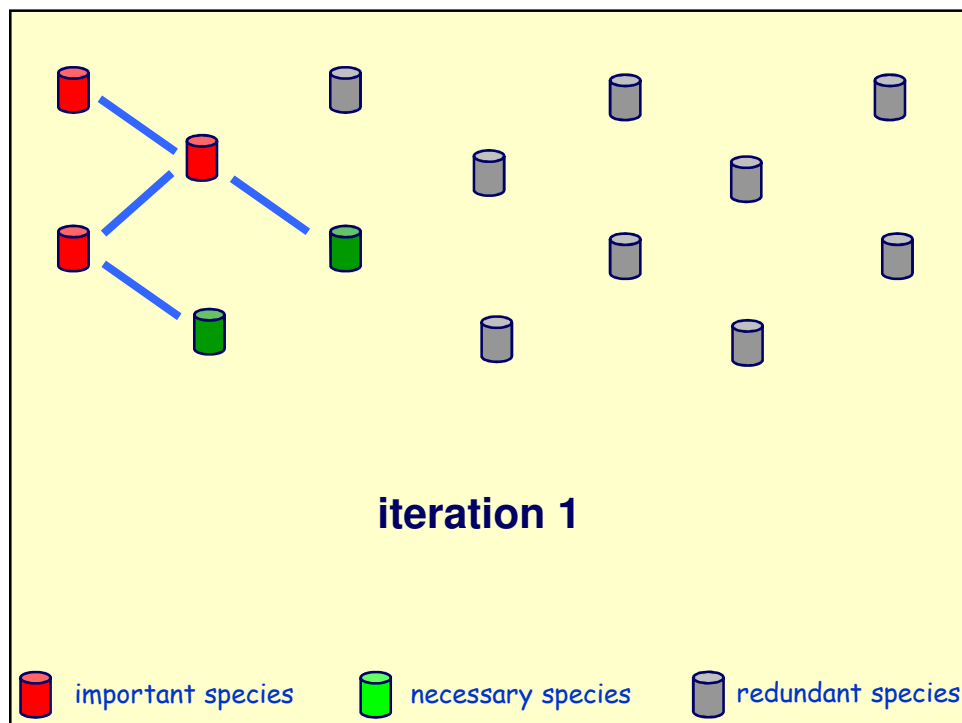
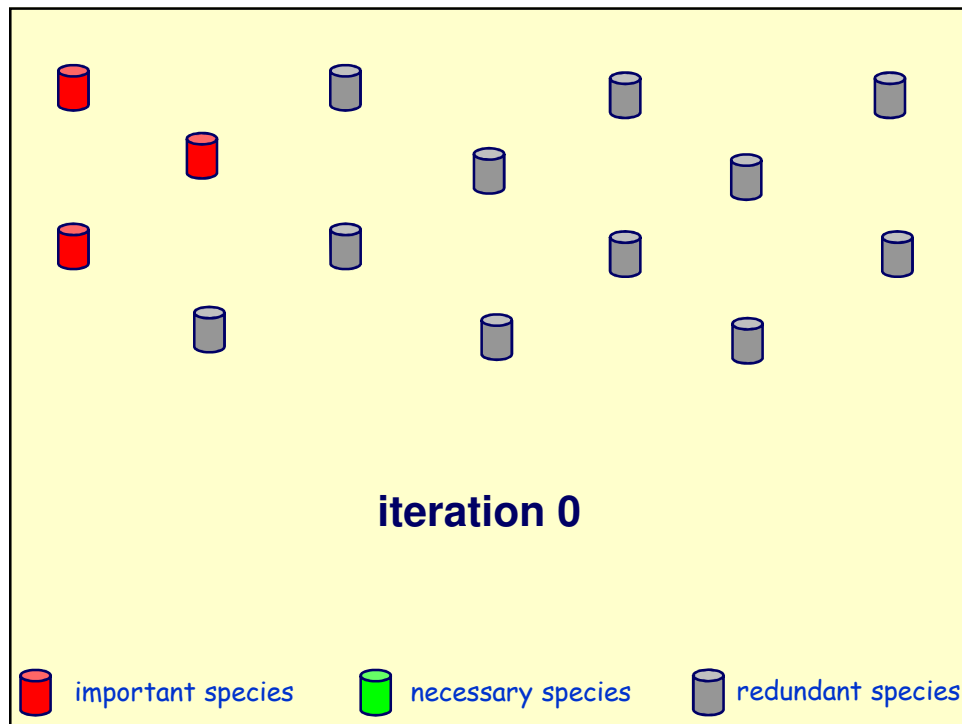
### Redundant species

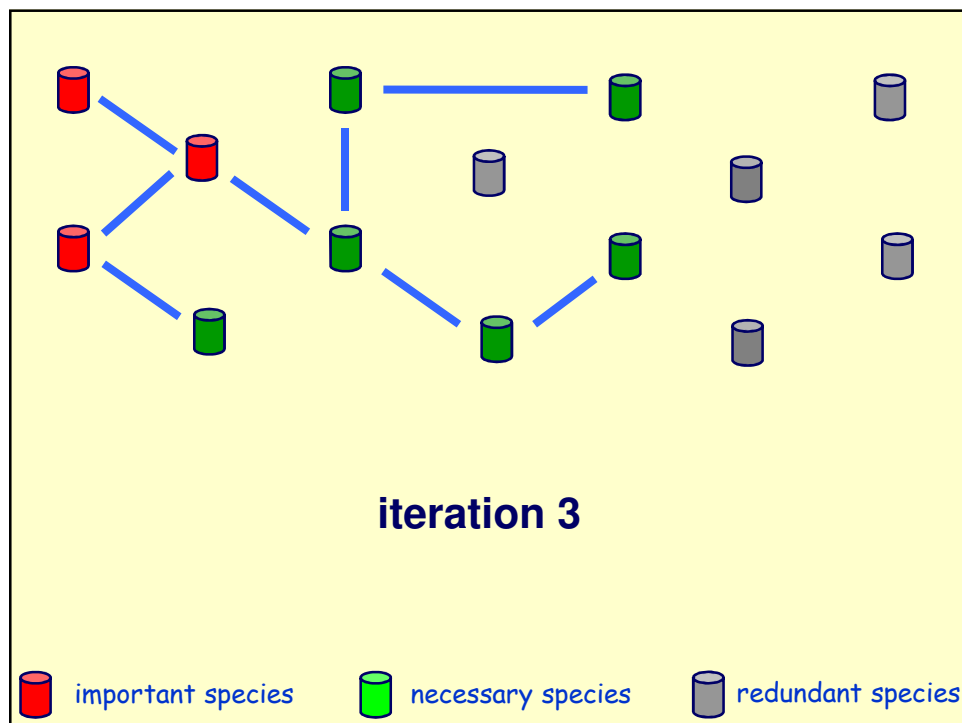
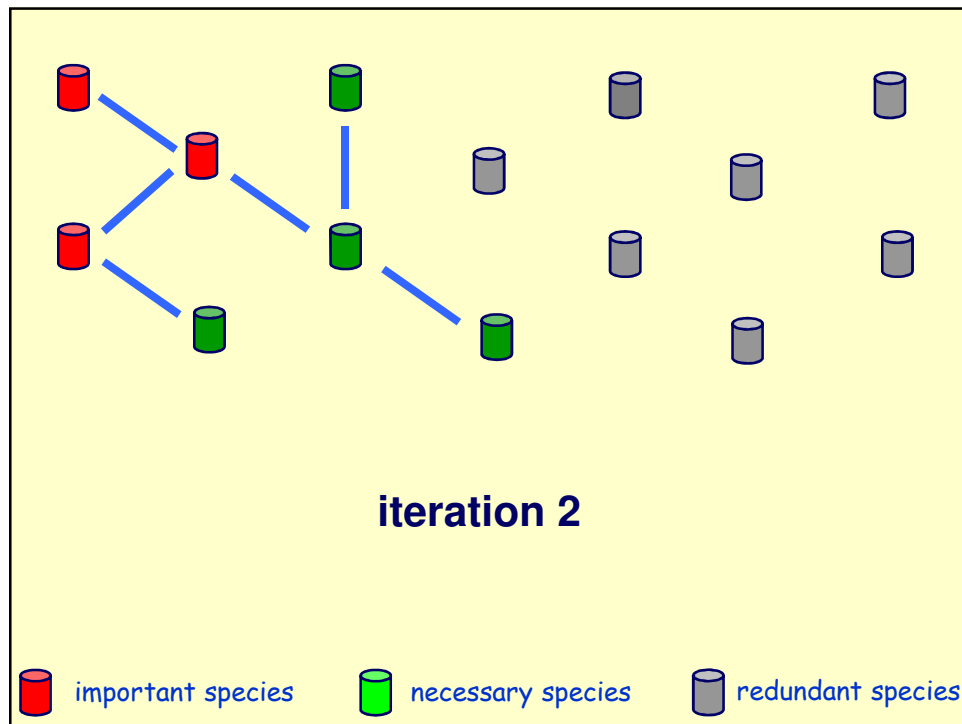
Species that are not important and not necessary

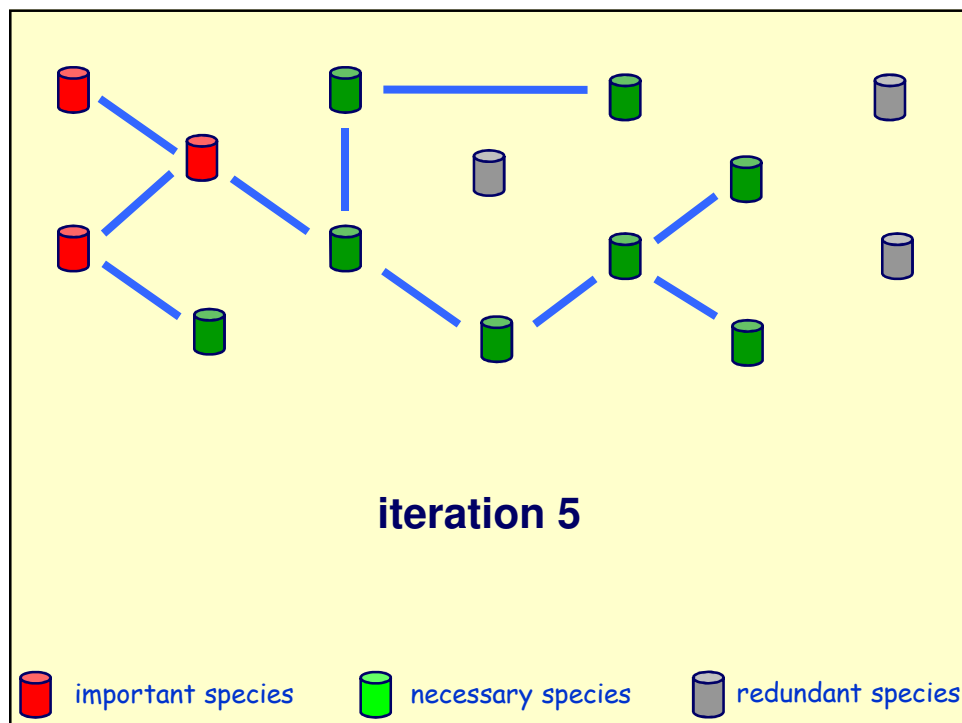
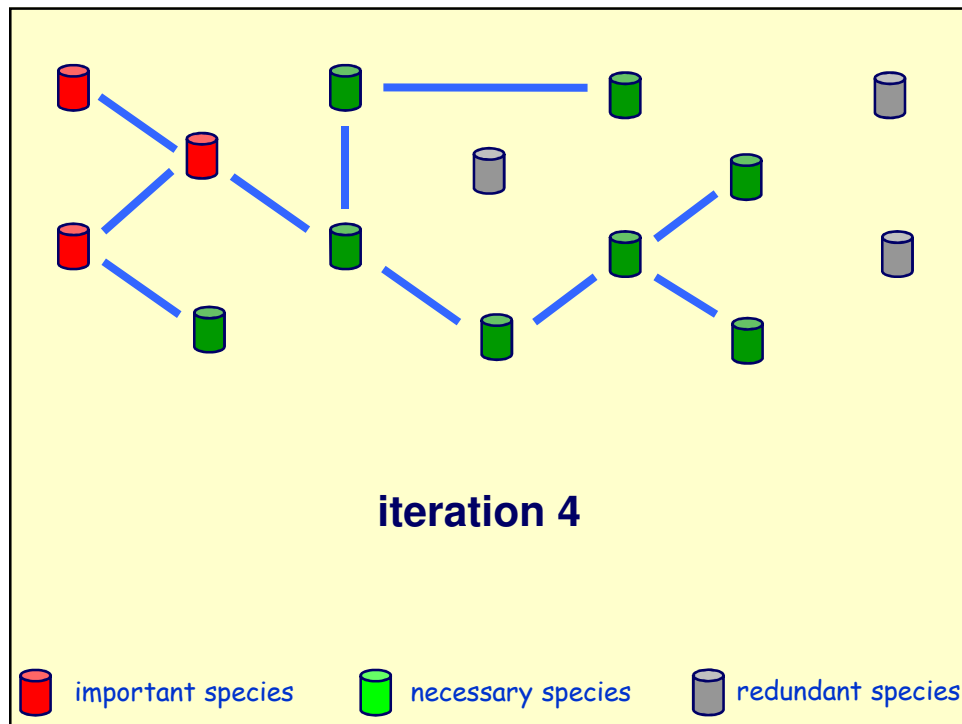
There are several methods, which start from the important species and look for the other species that are in close connection to the important species. The next step is looking for the species that are strongly coupled with the previous group etc.

**The redundant species are identified in an iteration.**









**Example:****gas-phase chemistry in solid-oxide fuel cells  
the partial oxidation of methane**

**Solid-oxide fuel cells (SOFCs):** power source for electric-driven vehicles.

Can be operated with hydrocarbon fuels.

Air is added to the hydrocarbon fuel to prevent deposit formation.

⇒ slow partial oxidation of the hydrocarbon before reaching the anode

**Dean mechanism:** homogeneous gas-phase chemistry  
in the anode channel of natural gas fuelled SOFCs.  
Partial oxidation of methane up to high conversion.

Reduction is needed for **computer optimization**  
of fuel cell geometry and operating conditions.

**Gas-phase chemistry in solid-oxide fuel cells:  
partial oxidation of methane 2**

Full Dean mechanism: 345 species and 6874 irreversible reactions.

It was investigated at a typical set of SOFC conditions:

$T = 900\text{ }^{\circ}\text{C}$  (1173.15 K)

$p = 1\text{ atm}$  (101325 Pa)

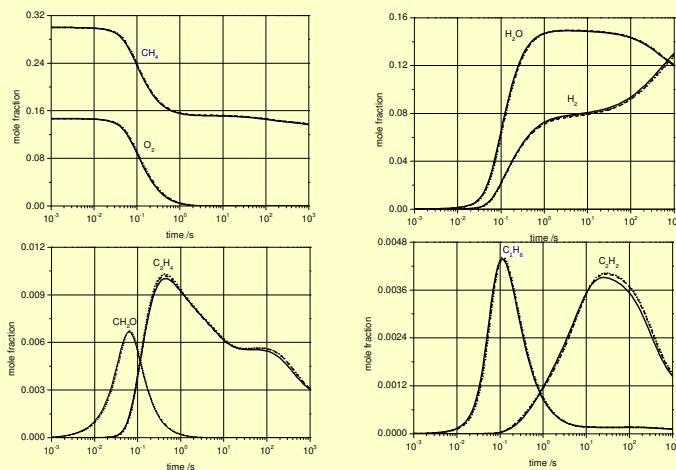
isothermal and isobaric conditions

30.0 % v/v methane and 70.0 % v/v air

**12 important species:**

$\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_6\text{H}_6$ .  
(the mole fraction of these species exceed 0.001)

## Testing the obtained reduced mechanisms



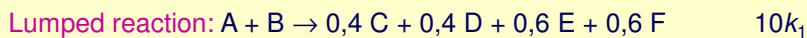
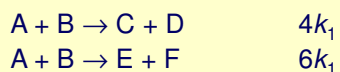
— full mechanism  
 - - - result of SEM-CM  
 ..... result of SEM-CM+ SEM-PCAF

6,874 reactions of 345 species  
 613 reactions of 47 species  
 297 reactions of 47 species

**Almost identical concentrations can be obtained with a much smaller mechanism!**

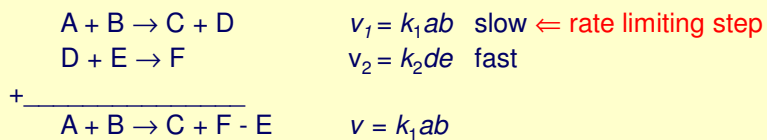
## Reaction lumping

### Lumping parallel reaction pathways



It generates exactly the same kinetic system of ODEs  
 Computer time is not saved

### Reaction lumping based on the rate limiting step



Less stiff ODEs, computer time is saved

## Species lumping

The mathematical definitions:

$$\frac{d\mathbf{Y}}{dt} = \mathbf{f}(\mathbf{Y})$$

Original kinetic system of ODEs,  
dimension of  $\mathbf{Y}$  is  $n$

$$\frac{d\hat{\mathbf{Y}}}{dt} = \hat{\mathbf{f}}(\hat{\mathbf{Y}})$$

ODE for the lumped variables  
dimension  $n' \leq n$

$$\hat{\mathbf{Y}} = \mathbf{h}(\mathbf{Y})$$

Definition of lumped variables

$\mathbf{h}$  linear function

$\Rightarrow$  linear lumping

$\mathbf{h}$  nonlinear function

$\Rightarrow$  nonlinear lumping

identical solutions

$\Rightarrow$  exact lumping

almost identical solutions  $\Rightarrow$  approximate lumping

$\mathbf{Y}, \hat{\mathbf{Y}}$  some elements of these two vectors are identical  
 $\Rightarrow$  constrained lumping

## Linear species lumping

$$\hat{\mathbf{Y}} = \mathbf{M}\mathbf{Y}$$

New variables are obtained by multiplying the  
original variable vector with a matrix

$$\mathbf{Y} = \mathbf{M}^{-1}\hat{\mathbf{Y}}$$

Regaining the original concentrations

$\mathbf{M}$

Lumping matrix ( $n \times n'$ )

Jacobian is constant

(= first order reactions only)

$\Rightarrow$  exact lumping is possible

Jacobian is not constant

$\Rightarrow$  no exact lumping

methods for approximate lumping  
do not work well

## Species lumping – a chemical approach

Lumping is frequently used in an intuitive way  
„chemical approach”

If species with similar reactions and reactivity are present:

- ⇒ these species are lumped
- ⇒ concentration of the lumped species  
= sum of the concentrations of the member species

called as the „*family method*” in atmospheric chemistry

A more involved approach:

the reactivity of the member species are different  
concentration of the lumped species  
= **weighted** sum of the concentrations of the member species

## n-heptane primary oxidation reactions

### Detailed Scheme

**135 Primary reactions**

**38 Intermediate radicals**

**30 Primary products**  
(retaining nC<sub>7</sub> structure)

3 n-heptenes  
8 cyclic-ethers  
4 hydroperoxides  
15 keto-hydroperoxides

### Lumped Scheme

**15 Primary lumped reactions**

**4 Intermediate lumped radicals**

**4 Primary lumped products**

1 lumped n-heptene  
1 lumped cyclic-ether  
1 lumped hydroperoxide  
1 lumped keto-hydroperoxide

# Mechanism reduction based on time scale analysis

## Quasi-steady-state approximation (QSSA)

The original kinetic system of differential equations:

$$d\mathbf{c}/dt = \mathbf{f}(\mathbf{c}, \mathbf{k}), \quad \mathbf{c}(0) = \mathbf{c}_0$$

The concentration vector is divided to two parts:

$\mathbf{c}^{(1)}$  concentration vector of non-QSSA species

$\mathbf{c}^{(2)}$  concentration vector of QSSA species

The Jacobian:

$$\mathbf{J} = \begin{pmatrix} \mathbf{J}^{(11)} & \mathbf{J}^{(12)} \\ \mathbf{J}^{(21)} & \mathbf{J}^{(22)} \end{pmatrix} = \begin{pmatrix} \partial \mathbf{f}^{(1)} / \partial \mathbf{c}^{(1)} & \partial \mathbf{f}^{(1)} / \partial \mathbf{c}^{(2)} \\ \partial \mathbf{f}^{(2)} / \partial \mathbf{c}^{(1)} & \partial \mathbf{f}^{(2)} / \partial \mathbf{c}^{(2)} \end{pmatrix}$$

Quasi-steady-state approximation:

$$d\mathbf{c}^{(1)}/dt = \mathbf{f}^{(1)}(\mathbf{c}, \mathbf{k})$$

$$\mathbf{0} = \mathbf{f}^{(2)}(\mathbf{c}, \mathbf{k})$$

$$\mathbf{c}(0) = \mathbf{c}_0$$

$\Leftarrow$  denote  $\mathbf{C}^{(2)}$  the concentration vector  
calculated from the  
algebraic equation



## The local error of the QSSA

$$\Delta \mathbf{c} = \mathbf{c}^{(2)} - \mathbf{C}^{(2)} \quad \text{Local error of the QSSA}$$

Taylor expansion of the production rate of the QSSA species at the QSSA concentrations:

$$\frac{d\mathbf{c}^{(2)}}{dt} = \underbrace{\mathbf{f}^{(2)}(\mathbf{c}, \mathbf{k})}_{\mathbf{0}} \Big|_{\mathbf{c}=\mathbf{C}} + \mathbf{J}^{(22)} \Delta \mathbf{c}^{(2)}$$

Calculation of the local error for several QSSA species:

$$d\mathbf{c}^{(2)}/dt = \mathbf{J}^{(22)} \Delta \mathbf{c}^{(2)}$$

Calculation of the local error for a single QSSA species:

$$\frac{dc_i}{dt} = J_{ii} \Delta c_i \quad \Rightarrow \quad -\Delta c_i = \left( \frac{-1}{J_{ii}} \right) \frac{dc_i}{dt}$$

**Error of QSSA approximation = lifetime × production rate of the species**

## Direct calculation of slow manifolds

$\mathbf{y}^M$  a point „on the surface” of the manifold

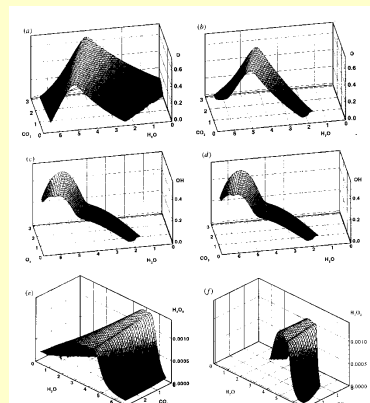
$\mathbf{f}(\mathbf{y}^M)$  velocity of the point „on the surface” of the manifold

$\mathbf{W}_s$  tangent plane of the manifold in this point (includes vector  $\mathbf{f}$ )

$\mathbf{W}_f$  vector of fast directions linearly independent of  $\mathbf{W}_s$

$\mathbf{f}(\mathbf{y}^M)$  this vector is orthogonal to the  $\mathbf{W}_f$  vectors:

$$\mathbf{W}_f \mathbf{f}(\mathbf{y}^M) = 0$$



1. Selection of the dimension (denote  $n_D$ )
2. Selection of  $n_D$  variables used for parameterization (vector  $\mathbf{x}$ ).  
The equation above defines all other concentrations that belong to the manifold as a function of vector  $\mathbf{x}$ .

**PROBLEM:** numerically ill-conditioned task, because vectors  $\mathbf{W}_f$  have frequently almost identical direction.

## Repromodelling

### Stages of reduction of a detailed reaction mechanism

original stiff ODE, many variables **SLOW SIMULATION**

→ making a **skeleton mechanism**  
(by elimination of redundant species and reactions, lumping)  
**FASTER**

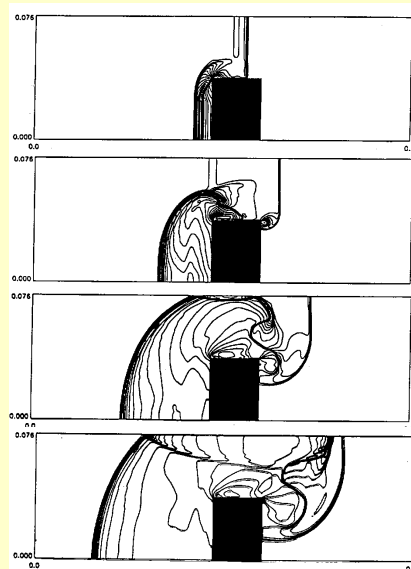
**skeleton mechanism** → manifold based mathematical model (ODE)

**skeleton mechanism** → difference equations obtained by the  
repromodelling method **FASTEST**

### Principle of repromodelling:

The chemical kinetic model is simulated several thousand times at different conditions. A polynomial is fitted to the simulation results. In the further simulations the fitted polynomial is used, instead of solving again the differential equations.

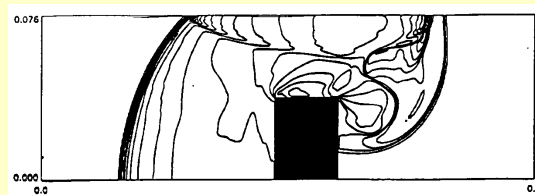
### Example: Spread of detonation wave in a $\text{H}_2/\text{O}_2/\text{Ar}$ mixture



## Spread of detonation wave in $\text{H}_2/\text{O}_2/\text{Ar}$ mixture



Calculated density map based on a detailed hydrogen combustion mechanism (9 variables)



Calculated density map based on a repromodel (polynomial approximation with 3 variables)

**100 times faster**

## Overview of mechanism reduction methods

### I. without time scale analysis

1. determination of a skeleton mechanism (a part of the original one)  
elimination of redundant species and reactions  
⇒ smaller kinetic system of ODEs
2. species lumping and reaction lumping  
⇒ smaller kinetic system of ODEs

### II. using time scale analysis

1. classic methods: QSSA and partial equilibrium  
⇒ smaller kinetic system of ODEs or  
coupled differential/algebraic equations
2. slow manifolds  
⇒ smaller kinetic system of ODEs
3. reparamodelling  
⇒ difference equations

End of topic 2