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

Lecture 2-4
Time scale analysis

Tamás Turányi
Chemical Kinetics Laboratory
Institute of Chemistry, Eötvös Loránd University (ELTE), Budapest. Hungary
Lifetimes and time scales

Half life:
Time period needed for the concentration of a species to decrease to ½, 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:
\[ A \rightarrow P \]
\[ Y = Y_0 e^{-kt} \]

lifetime: \[ \tau = \frac{1}{k} \]

half life: \[ \tau_{1/2} = \frac{\ln 2}{k} \]

Several first order reactions (e.g. in photochemistry the reactions of an excited species):
\[ A \rightarrow P_1 \]
\[ \rightarrow P_2 \]
\[ \rightarrow P_3 \]
\[ Y = Y_0 e^{-(k_1 + k_2 + k_3)t} \]

lifetime: \[ \tau = \frac{1}{(k_1 + k_2 + k_3)^2} \]
Lifetime

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

\[ P_i \quad \text{effect of producing steps} \]
\[ L_i \quad \text{effect of consuming steps} \]

Production rate of \(Y_i\):
\[
\frac{dY_i}{dt} = P_i - L_i Y_i
\]

\(Y_i\) lifetime:
\[
\tau = \frac{1}{L_i}
\]

General reaction mechanism:
\(Y_i\) lifetime:
\[
\tau = -\frac{1}{j_{ii}} \quad \text{where} \quad j_{ii} = \frac{\partial f_i}{\partial Y_i}
\]

\(j_{ii}\) is the \(i^{th}\) diagonal element of the Jacobian
Example

A → B \quad k_1

A + C → D \quad k_2

B → A \quad k_3

Production rate of species A:

\[
d a/d t = -k_1 a - k_2 ac + k_3 b
\]

\[
d a/d t = k_3 b - (k_1 + k_2 c) a
\]

"Atmospheric chemical" lifetime:

\[
d Y_i/d t = P_i - L_i Y_i \quad \tau_A = 1/L_A = 1/(k_1 + k_2 c)
\]

General lifetime:

\[
j_{AA} = \frac{\partial (d a/d t)}{\partial a} = -(k_1 + k_2 c) \quad \tau_A = -1/j_{AA} = 1/(k_1 + k_2 c)
\]
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:

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

short lifetime species = the effect of perturbation decreases rapidly = the perturbed trajectory converges very fast to 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 ($dY_i/d\ t$)
Eigenvector-eigenvalue decomposition of the Jacobian

\[ \Lambda = W J V \]

\[ J = \begin{pmatrix} \frac{\partial f_i}{\partial Y_j} \end{pmatrix} \]

- \( \Lambda \): diagonal matrix that contains the eigenvalues (complex eigenvalues!)
- \( W \): matrix of left eigenvectors (row vectors)
- \( V \): matrix of right eigenvectors (column vectors)

- denote \( W_f \) 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:

\[ I = W V \quad I = V W \]

therefore:

\[ J = V \Lambda W \]
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 \( S_1 \)

\[
S_1 = \frac{1}{\min_i |\text{Re}(\lambda_i)|} / \frac{1}{\max_i |\text{Re}(\lambda_i)|}
\]
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 $S_2$

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

characteristic time scale shortest time scale

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

$\tau$ 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
\[ \frac{d Y}{d t} = f(Y, p) \]

in the stationary point
\[ \frac{d Y}{d t} = 0 \]

**Stable stationary point:** we move it out, goes back

\[ J = \begin{bmatrix} \frac{\partial f_i}{\partial y_j} \end{bmatrix} \]

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

\[ \frac{dY}{dt} = f(Y, p) \]

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

\[ J = \begin{bmatrix} \frac{\partial f_1}{\partial y_1} \\ \vdots \\ \frac{\partial f_n}{\partial y_n} \end{bmatrix} \] the real parts of all eigenvalues are negative

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

The 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

Assume that the manifolds are attracting
(no strong autocatalysis, no explosion)
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
Calculated slow manifolds in combustion systems

O Gicquel et al.
Modes

Previous assumption: „The concentration of a single species is changed by $\Delta y_i$, and the concentrations of the other species are not changed”
This is approximately true if the concentration of the changed species is low and its lifetime is short.

Usually changing the concentration of a single species induces the change of the concentrations of several other species.

⇒ A more general approach:
the concentrations of several species are changed simultaneously by $\Delta Y$

linear approach
to the change of the perturbation:

$$\frac{d(\Delta Y)}{dt} \approx \frac{\partial f}{\partial Y} \Delta Y = J\Delta Y$$

The solution of this ODE: (assuming that the Jacobian does not change during the short time of relaxation)

$$\Delta Y(t) = e^{J\tau} \Delta Y(t_1)$$

$\Rightarrow$  

$$\Delta Y_i = C_1 e^{\lambda_1 \tau} + C_2 e^{\lambda_2 \tau} + C_3 e^{\lambda_3 \tau} + \ldots + C_n e^{\lambda_n \tau}$$

where $\tau = t - t_1$ is the elapsed time from the start of perturbation
Modes 2

introducing new variables: \( z \) vector of modes
c.f. normal coordinates in spectroscopy

calculation of mode \( z_i \):
\[
z_i = w_i \cdot Y
\]
where \( w_i \) is the \( i \)-th row of matrix \( W \)

calculation of concentration \( y_i \):
\[
Y_i = v_i \cdot z
\]
where \( v_i \) is the \( i \)-th column of matrix \( V \)

the transformed kinetic system of ODEs:
\[
\frac{dz}{dt} = W \cdot f(Vz), \quad z_0 = W \cdot Y_0
\]

If perturbation \( \Delta Y \) is towards direction \( w_1 \), then \( z_1 \neq 0 \), but for all the other \( j \) directions \( z_j = 0 \).

The change of \( z_i \) after perturbation:
\[
\Delta z_i(t) = \Delta z_i^0 \cdot e^{\lambda_i t}
\]

**IMPORTANT:** the Jacobian changes in the space of concentrations, therefore transformation \( Y \rightarrow z \) also changes with \( Y \)!
Modes 3

Denote $z_f$ the fast modes:

$$\tilde{Y}(t) = Y(t) + \Delta Y(t)$$

$$\frac{d\tilde{Y}}{dt} = \frac{d(Y + \Delta Y)}{dt} = f(Y, p) + \frac{d\Delta Y}{dt}$$

$$\frac{dz}{dt} = W f(\nabla z), \quad z_0 = W Y_0$$

$$\frac{d z_i}{dt} = w_i f = w_i f(Y^m) + w_i \frac{d\Delta Y}{dt} = \frac{d\Delta z_i}{dt}$$

Let $i$ belong to a fast mode and let $Y^m$ be a point on the manifold.

Therefore, for mode $i$:

$$\frac{d\Delta z_i}{dt} = w_i f$$
The modes can be perturbed independently from each other:

$$\frac{d \Delta z_i}{dt} = \lambda_i \Delta z_i$$

Comparing the two equations above:

$$w_i f = \lambda_i \Delta z_i$$

$$\Delta z_i = w_i f / \lambda_i$$

where $\Delta z_i$ is the distance from manifold $i$

Calculation of the dynamical dimension

\[ \Delta z_i = w_i f / \lambda_i \]

\[ \Delta z_i \] distance from the slow manifold towards direction \( w_j \)

If \( |\Delta z_i| < z_{\text{threshold}} \) \( \Rightarrow \) this mode is (almost) on the manifold

Assume that there are \( n_r \) modes
relaxed onto the corresponding slow manifold.

\( n \quad \) number of variables in the model
\( n_c \quad \) number of conserved properties
\( = \) number of zero eigenvalues of the Jacobian
\( n_r \quad \) number of relaxed modes

**actual dynamical dimension:** \( n_D = n - n_c - n_r \)
Change of the dynamical dimension during the course of a chemical reaction

\( n \) number of species in the mechanism
\( n_c \) number of conserved properties
  \((e.g. \ \text{number of elements in a closed system})\)

If the initial composition is randomly selected, initially the trajectory is moving in a \((n - n_c)\) dimensional space 
\((\text{change of elementary composition by chemical reactions is forbidden})\)

If all eigenvalues of the Jacobian are negative:
- all manifolds are attractive
- the actual dynamical dimension is continuously decreasing
- finally it \( nD= 1 \) (moving along a line) and the \( nD=0 \) (equilibrium point)

If some eigenvalue(s) of the Jacobian are positive:
- some manifolds are repellent
- the actual dynamical dimension is increasing
- the case of autocatalytic runaways (including explosions)
Change of dimension during adiabatic hydrogen/air explosion

grey region: here the largest eigenvalue is positive

- $n$: number of variables in the model
- $n_c$: number of conserved properties = number of zero eigenvalues of the Jacobian
- $n_r$: number of relaxed modes

actual dynamical dimension: $n_D = n - n_c - n_r$
Change of protein concentrations during a cell cycle

![Graph showing the change of protein concentrations during a cell cycle.](image-url)
Concentration changes are affected by the excitation periods.
Calculation the the dynamic dimension 2

\( n \)  number of ODE variables
\( n_c \)  number of conserved properties
= number of the zero eigenvalues of the Jacobian
\( n_r \)  number of relaxed modes

Actual dynamical dimension: \( n_D = n - n_c - n_r \)
Simulation of spatially inhomogeneous system described by a system of partial differential equations (PDEs)

Direct numerical solution of the PDE is feasible for small systems only.

A usually applied method is operator splitting

Chemistry and advection/diffusion are simulated separately:
- one time step with advection+diffusion (PDE solver)
- one time step with chemistry (ODE solver)

\[
\frac{dc(r, t)}{dt} = f(r, t, c) + \Theta(r, t, c, \nabla c, \nabla^2 c)
\]

- allows the application of special efficient PDE and ODE solvers.
- numerical tests show that operator splitting introduce little error
- allows the separate assessment of the CPU time needed for the simulation of chemistry and advection/diffusion

⇒ most of the computer time (e.g. 99%) is used for solving the chemical kinetic equations
History of the quasi-steady state approximation

1913 – 1960: analytical solution of the kinetic ODEs
   Bodenstein (1913): analytical solution to the equations of the $\text{H}_2/\text{Br}_2$ reaction system
   Szemjonov (1939): applied the QSSA for a part of the intermediates only

1960 – 1971: conversion of the stiff ODEs to non-stiff ODEs
   Edelson (1973) claimed that the stiff ODEs can already be solved directly (no need for the QSSA); nobody can assess the error introduced by the application of the QSSA $\Rightarrow$ QSSA should be banned

1971 – : production of skeleton models from detailed mechanisms for solving PDEs
   theoretical study of the QSSA method: (about 60 articles)
   main lines:
   • justification of the application of QSSA for small mechanisms
   • singular perturbation: analytical investigation of small systems

An early general article and its commented English translation.
   We developed this line further, see the following coming pages.

D. A. Frank-Kamenetskii: Условия применимости метода Боденштейна в химической кинетике
   (Conditions for the applicability of the Bodenstein method in chemical kinetics)
   Ж. Физ. Хим. (Zh. Fiz. Him.) 14, 695-700 (1940)

Quasi-steady-state approximation (QSSA)

The original kinetic system of differential equations:

\[
d \mathbf{c}/d \tau = f(C, k), \quad \mathbf{c}(0) = \mathbf{c}_0
\]

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:

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

Quasi-steady-state approximation:

\[
d \mathbf{c}^{(1)}/d \tau = f^{(1)}(C, k)
\]
\[
0 = f^{(2)}(C, k)
\]
\[
\mathbf{c}(0) = \mathbf{c}_0
\]

\(\Leftarrow\) denote \(\mathbf{C}^{(2)}\) the concentration vector calculated from the algebraic equation
The local error of the QSSA

\[ \Delta c = c^{(2)} - C^{(2)} \]

Local error of the QSSA

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

\[ \frac{d c^{(2)}}{dt} = f^{(2)}(c, k)igg|_{c=C} + J^{(22)} \Delta c^{(2)} \]

Calculation of the local error for several QSSA species:

\[ d c^{(2)}/d t = J^{(22)} \Delta c^{(2)} \]

Calculation of the local error for a single QSSA species:

\[ \frac{d c_i}{dt} = J_{ii} \Delta c_i \Rightarrow - \Delta c_i = \left( \frac{-1}{J_{ii}} \right) \frac{d c_i}{d t} \]

error of QSSA approximation = lifetime \times production rate of the species

Example: QSSA error at methane pyrolysis

The QSSA local error of each species at 50 s

<table>
<thead>
<tr>
<th>Species</th>
<th>Relative Error</th>
<th>Absolute Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>19. CH₃</td>
<td>-6.200E-01 %</td>
<td>-2.631E-13 mole/cm³</td>
</tr>
<tr>
<td>20. CH₃CH₂CH₃</td>
<td>-5.284E-01 %</td>
<td>-4.568E-14 mole/cm³</td>
</tr>
<tr>
<td>21. CH.CHCH₂CH₃</td>
<td>5.050E-01 %</td>
<td>3.022E-21 mole/cm³</td>
</tr>
<tr>
<td>22. (CH₃)₂C=CH.</td>
<td>4.889E-01 %</td>
<td>1.708E-19 mole/cm³</td>
</tr>
<tr>
<td>23. C₂H₅</td>
<td>4.013E-01 %</td>
<td>2.989E-16 mole/cm³</td>
</tr>
<tr>
<td>24. CH≡CCH₂ .</td>
<td>-3.385E-01 %</td>
<td>-4.109E-14 mole/cm³</td>
</tr>
<tr>
<td>25. CH₂=CHCH=CH₂</td>
<td>3.062E-01 %</td>
<td>8.733E-13 mole/cm³</td>
</tr>
<tr>
<td>26. CH.CHCH₃</td>
<td>3.030E-01 %</td>
<td>4.148E-18 mole/cm³</td>
</tr>
<tr>
<td>27. C₂H₃</td>
<td>2.612E-01 %</td>
<td>1.241E-16 mole/cm³</td>
</tr>
<tr>
<td>28. CH₂=CHCH₂ .</td>
<td>2.134E-01 %</td>
<td>1.153E-14 mole/cm³</td>
</tr>
<tr>
<td>29. CH≡CCH₃</td>
<td>-2.040E-01 %</td>
<td>-1.283E-11 mole/cm³</td>
</tr>
<tr>
<td>30. CH₂</td>
<td>1.591E-01 %</td>
<td>1.041E-20 mole/cm³</td>
</tr>
<tr>
<td>31. C</td>
<td>-1.366E-01 %</td>
<td>-8.633E-30 mole/cm³</td>
</tr>
<tr>
<td>32. CH₂=C.CH₃</td>
<td>1.364E-01 %</td>
<td>5.094E-18 mole/cm³</td>
</tr>
<tr>
<td>33. CH₂S</td>
<td>1.025E-01 %</td>
<td>5.811E-23 mole/cm³</td>
</tr>
<tr>
<td>34. H</td>
<td>7.083E-02 %</td>
<td>1.699E-16 mole/cm³</td>
</tr>
<tr>
<td>35. CH₂=C=CH₂</td>
<td>-6.929E-02 %</td>
<td>-1.209E-12 mole/cm³</td>
</tr>
</tbody>
</table>
Thank you for your attention!