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Reaction kinetics basics and local sensitivity analysis

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

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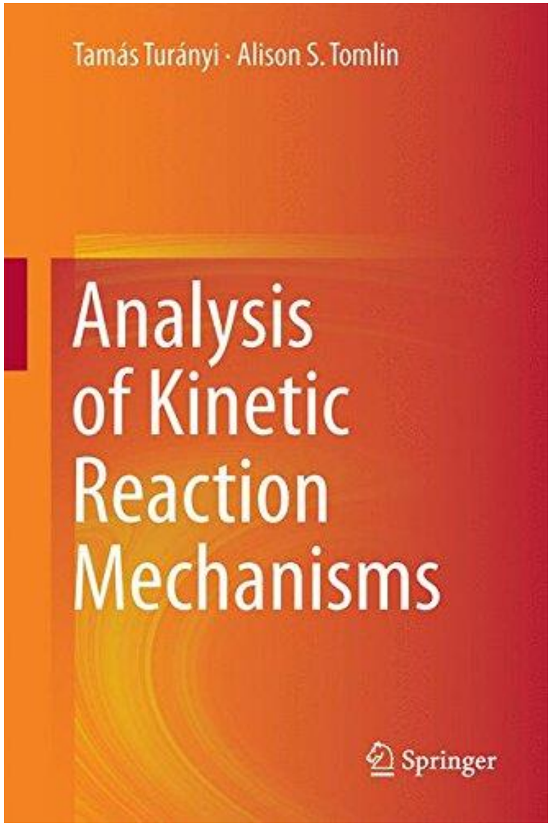
Analysis of kinetic reaction mechanisms – the book



Tamás Turányi and Alison S. Tomlin:

Analysis of Kinetic Reaction Mechanisms

Springer, 2014

(with 1025 references)

Web page:
http://garfield.chem.elte.hu/Turanyi/KineticReactionMechanisms.html

- table of contents
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Reaction kinetics basics

Characterization of chemical changes with a stoichiometric (overall) equation:

- properly indicates the ratio of reactants and products
- usually there is no such a real chemical process

$2\ H_2 + O_2 = 2\ H_2O$

$0 = -2\ H_2 - 1\ O_2 + 2\ H_2O$

$$0 = \sum_j \nu_j A_j$$

$\nu_1 = -2$ $\quad A_1 =$ „H_2”

$\nu_2 = -1$ $\quad A_2 =$ „O_2”

$\nu_3 = +2$ $\quad A_3 =$ „H_2O”

ν_j stoichiometric coefficient
(negative for reactants, positive for products)

Features:

- the order of the species is arbitrary
- the stoichiometric coefficients can be multiplied with the same real number

$H_2 + ½\ O_2 = H_2O$ is also a good overall equation

Reaction rate

production rate of a species:

$$\frac{\mathrm{d}\,Y_j}{\mathrm{d}\,t}$$

reaction rate:

$$r = \frac{1}{\nu_j}\frac{\mathrm{d}\,Y_j}{\mathrm{d}\,t}$$

Y_j is the molar concentration of species A_j *e.g.* [mole dm^{-3}]

in a small domain of concentrations always applicable: $r = k\prod_j Y_j^{\alpha_j}$,

k	rate coefficient
α_j	reaction order with respect species *j*
$\alpha = \sum_j \alpha_j$	overall reaction order

Complex reaction mechanisms

Almost always there are many simultaneous reaction steps:

$$\sum_j \nu_{ij}^L \, \mathrm{A}_j = \sum_j \nu_{ij}^R \, \mathrm{A}_j$$

A reaction step

can be an elementary reaction (physically occurs this way) or

can be a non-elementary reaction lumped from elementary reactions.

ν_{ij}^L matrix of left hand side stoichiometric coefficients

elementary: sum is not more than 2; zero or positive integer

non-elementary: zero or positive integer

ν_{ij}^R matrix of right hand side stoichiometric coefficients

elementary: sum is not more than 2; zero or positive integer

non-elementary: any real number (can be zero, negative, fraction)

$\Delta\nu_{ij} = \nu_{ij}^R - \nu_{ij}^L$ calculation of the (previous) stoichiometric matrix

Kinetic system of differential equations

law of mass action (Guldberg and Waage, 1865):

$$r_i = k_i \prod_j Y_j^{\nu_{ij}^L}$$

k_i	rate coefficient of reaction step *i*
r_i	rate of reaction step *i*

Definition of the kinetic system of differential equations:

$$\frac{\mathrm{d}Y_j}{\mathrm{d}t} = \sum_i \Delta\nu_{ij}\, r_i; \quad j = 1,\ 2,\ \ldots, n$$

The kinetic system of differential equations in matrix-vector form:

$$\frac{\mathrm{d}\mathbf{Y}}{\mathrm{d}t} = \boldsymbol{\nu}\,\mathbf{r}$$

Matrices to be mentioned frequently

Initial value problem in reaction kinetics:

$$\frac{\mathrm{d}\mathbf{Y}}{\mathrm{d}t} = \mathbf{f}(\mathbf{Y}, \mathbf{k}), \qquad \mathbf{Y}(t_0) = \mathbf{Y}_0$$

Jacobian:

$$\mathbf{J} = \left\{ \frac{\partial f_i}{\partial y_j} \right\}$$

The Jacobian usually changes with changing concentrations

matrix F:

$$\mathbf{F} = \left\{ \frac{\partial f_i}{\partial k_j} \right\}$$

also depends on the concentrations

Kinetic system of differential equations: an example

The Oregonator model of the Belousov-Zhabotinskii oscillating reaction:

1.	$X + Y \rightarrow 2\ P$	k_1	$r_1 = k_1xy$
2.	$Y + A \rightarrow X + P$	k_2	$r_2 = k_2ya$
3.	$2\ X \rightarrow P + A$	k_3	$r_3 = k_3x^2$
4.	$X + A \rightarrow 2\ X + 2\ Z$	k_4	$r_4 = k_4xa$
5.	$X + Z \rightarrow \boxed{0.5}\ X + A$	k_5	$r_5 = k_5xz$
6.	$Z + M \rightarrow Y \boxed{-} Z$	k_6	$r_6 = k_6zm$

$X = HBrO_2$
$Y = Br^-$
$Z = Ce^{4+}$
$A = BrO_3^-$
$P = HOBr$
M = malonic acid

The detailed 80-step reaction mechanism could be reduced to this 6 reaction step.

Note, that negative and fractional stoichiometric coefficients are present on the right hand side!

Kinetic system of differential equations: an example 2

$X = HBrO_2$	variable of a diff. equation
$Y = Br^-$	variable of a diff. equation
$Z = Ce^{4+}$	variable of a diff. equation
$A = BrO_3^-$	constant concentration
$P = HOBr$	product only
$M =$ malonic acid	constant concentration

1. $X + Y \rightarrow 2\,P$

2. $Y + A \rightarrow X + P$

3. $2\,X \rightarrow P + A$

4. $X + A \rightarrow 2\,X + 2\,Z$

5. $X + Z \rightarrow 0{,}5\,X + A$

6. $Z + M \rightarrow Y - Z$

$$\frac{\mathrm{d}\,x}{\mathrm{d}\,t} = -1\,r_1 + 1\,r_2 - 2\,r_3 + 1\,r_4 - 0{,}5\,r_5 \quad \Rightarrow \quad \frac{\mathrm{d}\,x}{\mathrm{d}\,t} = -k_1xy + k_2ya - 2k_3x^2 + k_4xa - 0{,}5\,k_5xy$$

$$\frac{\mathrm{d}\,y}{\mathrm{d}\,t} = -1\,r_1 - 1\,r_2 + 1\,r_6 \quad \Rightarrow \quad \frac{\mathrm{d}\,y}{\mathrm{d}\,t} = -k_1xy - k_2ya + k_6zm$$

$$\frac{\mathrm{d}\,z}{\mathrm{d}\,t} = +2\,r_4 - 1\,r_5 - 2\,r_6 \quad \Rightarrow \quad \frac{\mathrm{d}\,z}{\mathrm{d}\,t} = 2k_4xa - k_5xz - 2k_6zm$$

calculation of the Jacobian

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -k_1 xy + k_2 ya - 2k_3 x^2 + k_4 xa - 0.5k_5 xz$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = -k_1 xy - k_2 ya + k_6 zm$$

$$\frac{\mathrm{d}z}{\mathrm{d}t} = 2k_4 xa - k_5 xz - 2k_6 zm$$

$$\mathbf{J} = \left\{ \frac{\partial f_i}{\partial y_j} \right\}$$

$\frac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial x} = -k_1 y - 4k_3 x + k_4 a - 0{,}5k_5 z$	$\frac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial y} = -k_1 x + k_2 a$	$\frac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial z} = -0.5k_5 x$
$\frac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial x} = -k_1 y$	$\frac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial y} = -k_1 x - k_2 a$	$\frac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial z} = +k_6 m$
$\frac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial x} = 2k_4 a - k_5 z$	$\frac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial y} = 0$	$\frac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial z} = -k_5 x - 2k_6 m$

calculation of matrix F

$$\frac{\mathrm{d}\,x}{\mathrm{d}\,t} = -k_1xy + k_2ya - 2k_3x^2 + k_4xa - 0.5k_5xz$$

$$\frac{\mathrm{d}\,y}{\mathrm{d}\,t} = -k_1xy - k_2ya + k_6zm$$

$$\frac{\mathrm{d}\,z}{\mathrm{d}\,t} = 2k_4xa - k_5xz - 2k_6zm$$

$$\mathbf{F} = \left\{ \frac{\partial f_i}{\partial k_j} \right\}$$

$\frac{\partial \frac{\mathrm{d}\,x}{\mathrm{d}\,t}}{\partial k_1} = -xy$	$\frac{\partial \frac{\mathrm{d}\,x}{\mathrm{d}\,t}}{\partial k_2} = ya$	$\frac{\partial \frac{\mathrm{d}\,x}{\mathrm{d}\,t}}{\partial k_3} = -2x^2$	$\frac{\partial \frac{\mathrm{d}\,x}{\mathrm{d}\,t}}{\partial k_4} = xa$	$\frac{\partial \frac{\mathrm{d}\,x}{\mathrm{d}\,t}}{\partial k_5} = -0.5xz$	$\frac{\partial \frac{\mathrm{d}\,x}{\mathrm{d}\,t}}{\partial k_6} = 0$
$\frac{\partial \frac{\mathrm{d}\,y}{\mathrm{d}\,t}}{\partial k_1} = -xy$	$\frac{\partial \frac{\mathrm{d}\,y}{\mathrm{d}\,t}}{\partial k_2} = -ya$	$\frac{\partial \frac{\mathrm{d}\,y}{\mathrm{d}\,t}}{\partial k_3} = 0$	$\frac{\partial \frac{\mathrm{d}\,y}{\mathrm{d}\,t}}{\partial k_4} = 0$	$\frac{\partial \frac{\mathrm{d}\,y}{\mathrm{d}\,t}}{\partial k_5} = 0$	$\frac{\partial \frac{\mathrm{d}\,y}{\mathrm{d}\,t}}{\partial k_6} = zm$
$\frac{\partial \frac{\mathrm{d}\,z}{\mathrm{d}\,t}}{\partial k_1} = 0$	$\frac{\partial \frac{\mathrm{d}\,z}{\mathrm{d}\,t}}{\partial k_2} = 0$	$\frac{\partial \frac{\mathrm{d}\,z}{\mathrm{d}\,t}}{\partial k_3} = 0$	$\frac{\partial \frac{\mathrm{d}\,z}{\mathrm{d}\,t}}{\partial k_4} = 2xa$	$\frac{\partial \frac{\mathrm{d}\,z}{\mathrm{d}\,t}}{\partial k_5} = -xz$	$\frac{\partial \frac{\mathrm{d}\,z}{\mathrm{d}\,t}}{\partial k_6} = -2zm$

Properties of kinetic differential equations

- The system of differential equations contains only first order derivatives (dc / dt), which are usually nonlinear functions of the concentrations.

  ⇒ **first order nonlinear system of differential equations**

- In general, several other concentrations influence the production rate of each species.

  ⇒ **coupled differential equations**

- The reaction rates differ several orders of magnitude

  ⇒ **stiff differential equations**

- Simulation results of laboratory experiments do not depend on the wall clock time, **BUT** the results of atmospheric chemical models depend on the actual pressure, temperature and solar raditation ⇒ depend on the physical time.

  ⇒ **autonomous OR non-autonomous differential equations**

- Some laboratory reactions can be (approximately) spatially homogeneous, but outside the laboratories most chemical reactions are spatially inhomogeneous. In most cases the transport of species and heat have to be taken into account.

  ⇒ **partial system of differential equations, with chemical source term**

Conserved properties

Isolated system:
The total internal energy is constant

Constant volume closed system:
the sum of the concentrations is constant,
if each the change of the number of moles in each reaction step is zero.
e.g. for reaction $H_2 + Cl_2 = 2\,HCl$

Closed system, elementary reactions only:
the number of moles of the elements is constant.

The moles of moieties (*e.g.* benzene ring) can remain constant

Example for conserved properties in a C_2H_4,CH_4 , C_6H_6 mixture:
C-atom → $2\,[C_2H_4] + 1\,[CH_4] + 6\,[C_6H_6] = \text{constant}$
H-atom → $4\,[C_2H_4] + 4\,[CH_4] + 6\,[C_6H_6] = \text{constant}$

Some linear combinations of the concentrations are constant.

N conserved property:
⇒ the rank of the stoichiometric matrix is lower by *N*
⇒ the system can be simulated **exactly** with (n-N) variables

Temperature dependence of rate coefficient *k*

Described by the Arrhenius equation:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \qquad \ln k = \ln A - \frac{E_a}{RT}$$

A	preexponential factor
Ea	activation energy

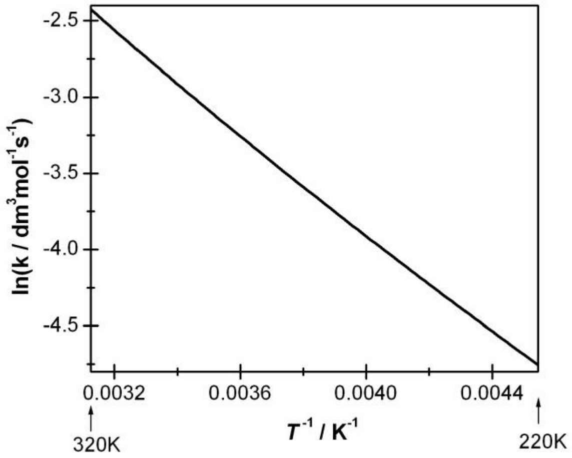
If the rate coefficient *k* is measured at several *T* temperatures and

ln *k* is plotted as a function of 1/*T*

the data fit to a line, if the (original) Arrhenius equation is valid

slope is $m = -E_a/R$ $\Rightarrow$ determination of E_a

Arrhenius plot:

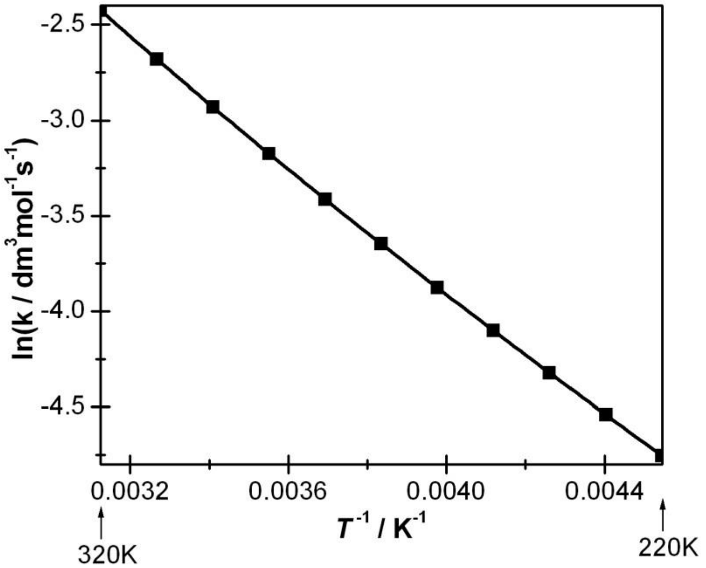


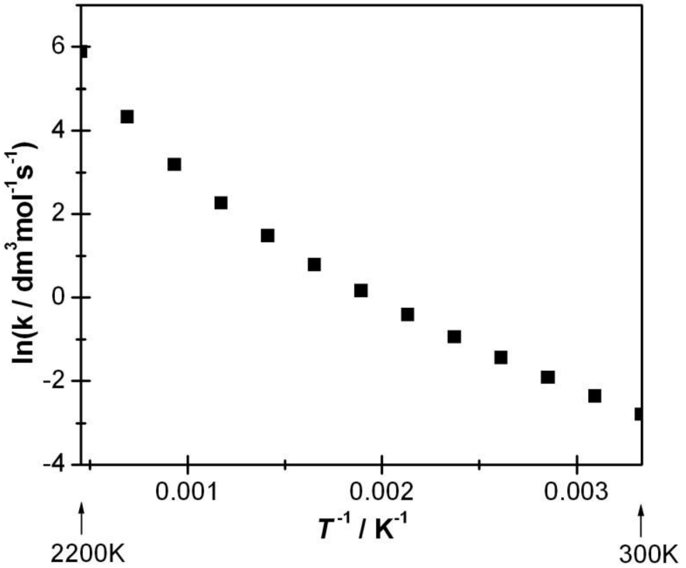
Example: reaction $CH_4 + OH \rightarrow CH_3 + H_2O$

- the most important methane consuming reaction step in the troposphere
- one of the most important steps at methane combustion

Arrhenius plot between 220 K (– 53 °C)
and 320 K (+ 47 °C)

Arrhenius plot between 300 K (27 °C)
and 2200 K (≈1930 °C)





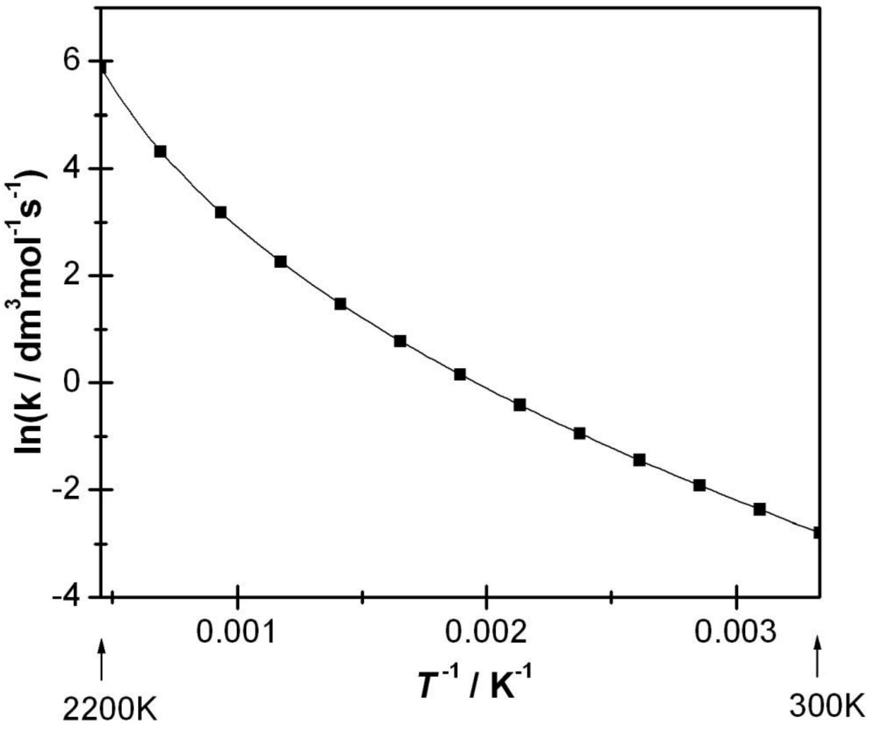
the Arrhenius equation is usually very accurate in a small (few times 10 K) temperature range.
(solution phase and atmospheric chemistry)

the original Arrhenius equation is usually not applicable in a wide temperature range
(combustion and pyrolytic systems)

Temperature dependence of the rate coefficient *2*

$$k = BT^{n}\,\mathrm{e}^{-\frac{C}{RT}}$$

extended Arrhenius equation



Important!
If $n \neq 0$. then $A \neq B$ and $E_a \neq C$

General definition of
activation energy:

$$E_a = -R\frac{\partial \ln k}{\partial\left(1/T\right)}$$

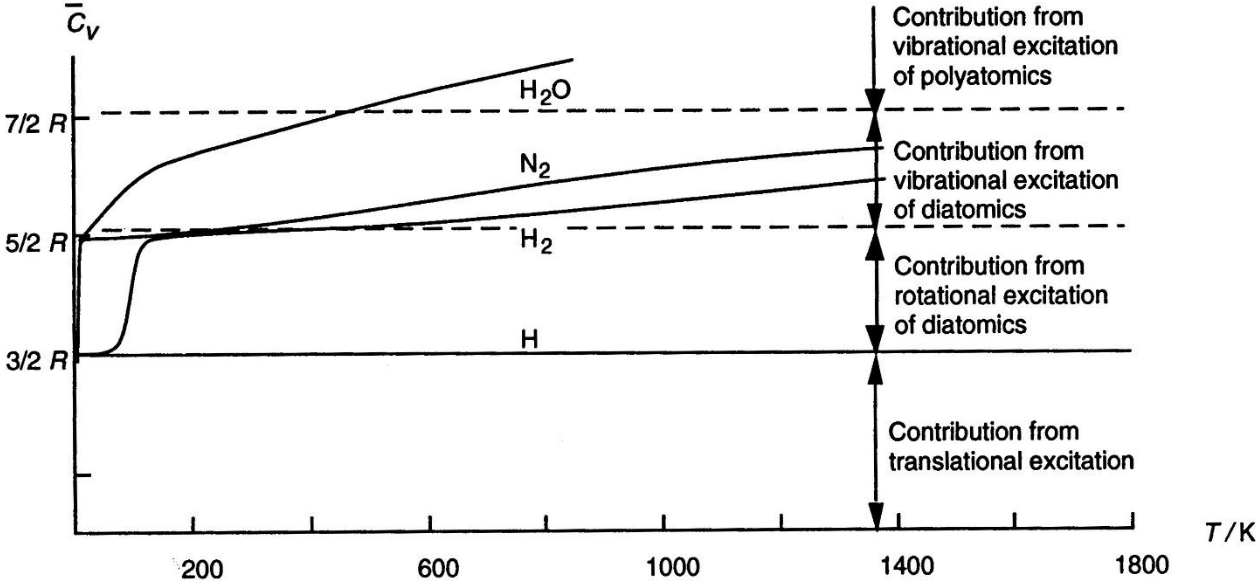
Temperature dependence of thermodynamic data

NASA polynomials

$$\frac{H^{\theta}}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$$

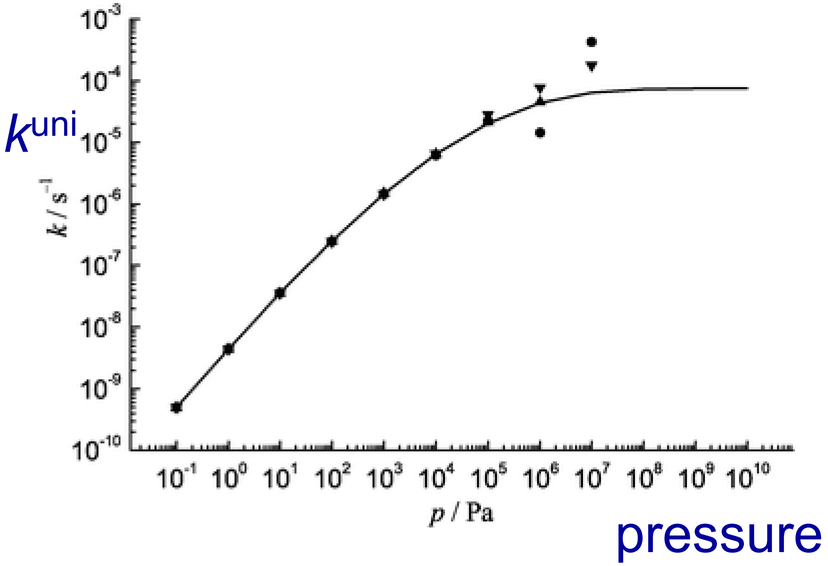
$$\frac{c_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$\frac{S^{\theta}}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7$$



Pressure dependence of the rate coefficients 1

unimolecular decomposition



decomposition or isomerization of a species

$$A + M = P + M$$

A	reactant
P	product
M	colliding partner for energy transfer

low pressure	2nd order decay of A
high pressure	1st order decay of A

„pseudo first order” rate coefficient:

high pressure limit: $k^{\mathrm{uni}} = k_\infty$

low pressure limit: $k^{\mathrm{uni}} = k_0\,[\mathrm{M}]$

The temperature dependences of k_0 and k_∞ are described independently by extended Arrhenus equations:

$$k_0 = A_0 T^{n_0} \exp\left(\frac{-E_0}{RT}\right) \qquad k_\infty = A_\infty T^{n_\infty} \exp\left(\frac{-E_\infty}{RT}\right)$$

Lindemann – Hinshelwood model

$A + M$	$\rightarrow A^* + M$	k_1
$A^* + M$	$\rightarrow A + M$	k_2
A^*	$\rightarrow P$	k_3

$$k_{\mathrm{uni}} = \frac{k_3 k_1 [M]}{k_2 [M] + k_3}$$

high pressure: $[M] \rightarrow \infty$ $\quad k_{\mathrm{uni}} \approx \frac{k_3 k_1}{k_2}$ $\quad k_\infty = \frac{k_3 k_1}{k_2}$

low pressure: $[M] \approx 0$ $\quad k_{\mathrm{uni}} \approx k_1 [M]$ $\quad k_0 = k_1$

unimolecular decomposition rates:

k^{uni} „pseudo first order” rate coefficient (s^{-1})

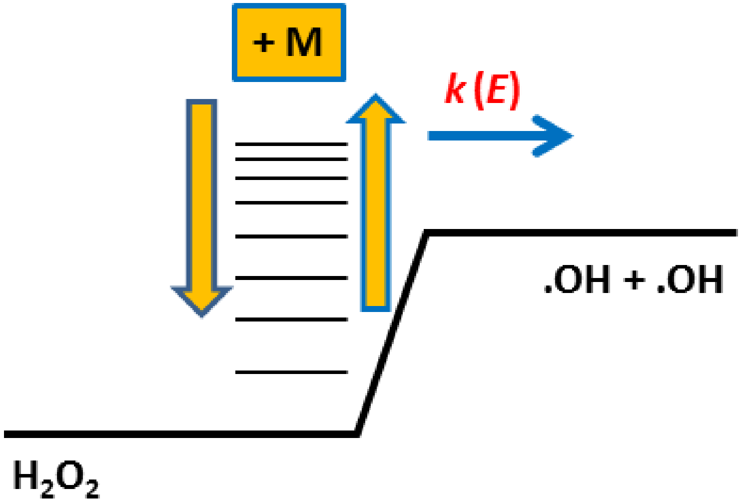
k_∞ high pressure limit (first order) rate coefficient (s^{-1})

k_0 low pressure limit (second order) rate coefficient ($mol^{-1}\ dm^3\ s^{-1}$)

Refined Lindemann – Hinshelwood model of unimolecular reactions

sample reaction: $H_2O_2 + M \rightarrow H_2O_2^* + M \rightarrow .OH + .OH + M$

- instead of assuming a single excited species, $H_2O_2^*$ exists in a range of different rovibrationally excited states.
- the rate of the decompostion step increases with the increasing rovibrational energy of $H_2O_2^*$



low pressure:

- the rate limiting is the collision with M
- the overall decomposition rate is proportional with pressure

high pressure:

- the rate limiting is the decomposition of $H_2O_2^*$
- the overall decomposition rate is independent of pressure

$H_2O_2 \rightarrow .OH + .OH$ 2nd order at low pressure, 1st order at high pressure

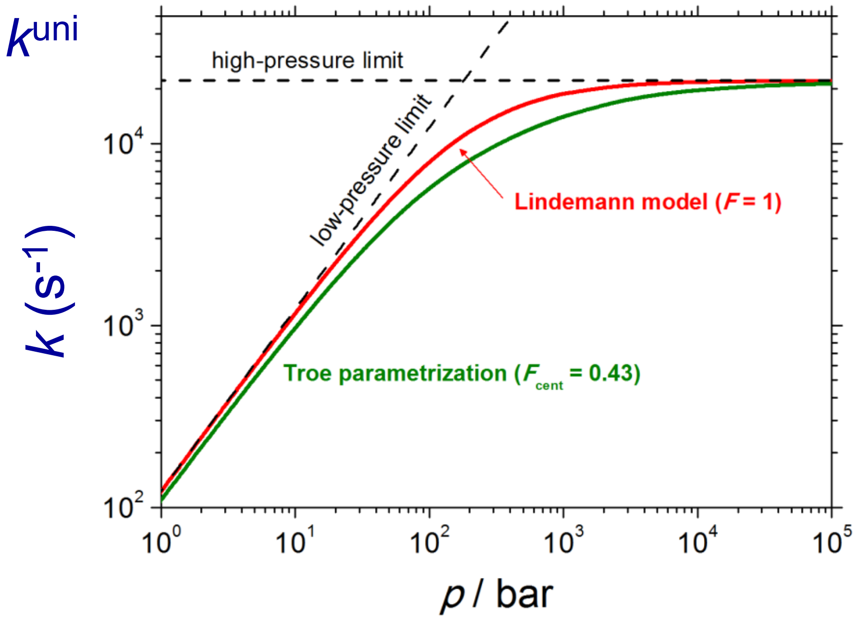
Unimolecular decomposition: calculation of the rate coefficient at an intermediate pressure

$$k = k_\infty \left(\frac{P_r}{1 + P_r} \right) F$$

$$P_r = \frac{k_0 [\mathrm{M}]}{k_\infty}$$

P_r reduced pressure
F controls the shape
of the $k(p)$ curve

$H_2O_2\ (+M) \rightarrow .OH + .OH\ (+M)$



in the Lindemann model $F = 1$

F can be defined as a function of pressure and temperature
(*e.g.* using Troe parameterization):

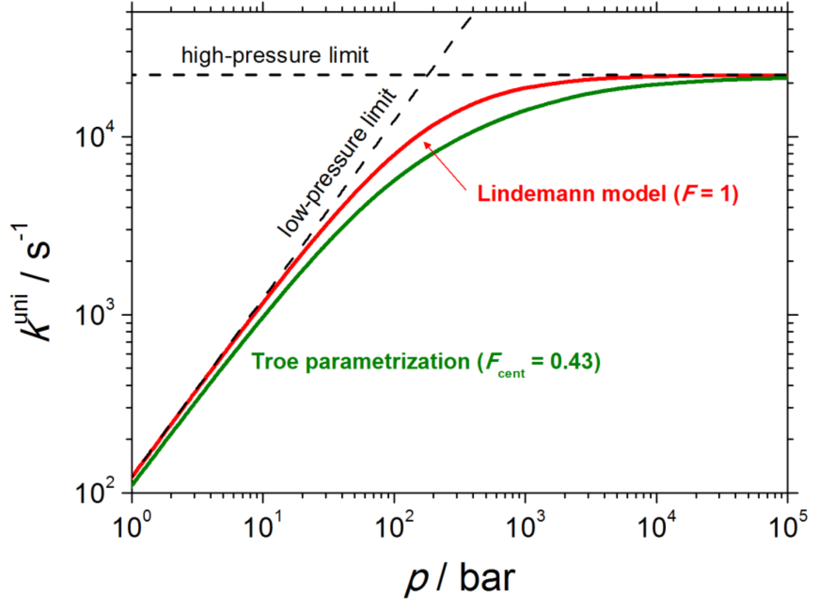
$$\log F = \log F_{\mathrm{cent}} \left[1 + \left[\frac{\log P_r + c}{n - d(\log P_r + c)} \right]^2 \right]^{-1}$$

$$c = -0.4 - 0.67 \log F_{\mathrm{cent}}$$
$$n = -0.75 - 1.271 \log F_{\mathrm{cent}}$$
$$d = 0.14$$

$$F_{cent} = (1 - \alpha) \exp\left(-\frac{T}{T^{***}} \right) + \alpha \exp\left(-\frac{T}{T^{*}} \right) + \exp\left(-\frac{T^{**}}{T} \right)$$

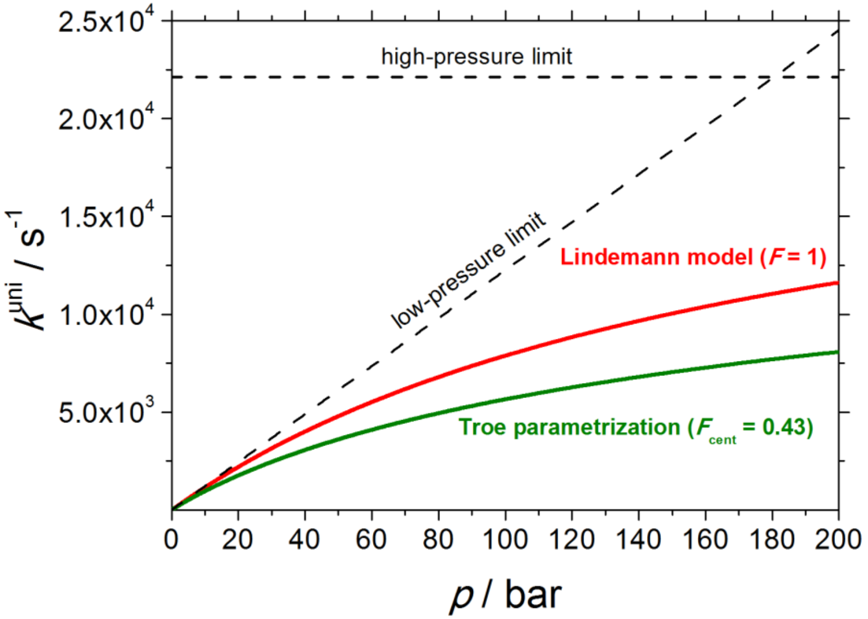
Reaction H_2O_2 (+M) → .OH + .OH (+M)

lg k^{uni} – lg p plot



***T* = 1000 K**

k^{uni} – p plot



source of data: J. Troe, *Combustion and Flame* **158,** 594–601 (2011)

Collision efficiency parameters

M any species present in the mixture
BUT some species are more effective colliders

good collider: removes much energy from the excited species in each collision

Which are the good colliders?
- species with similar energy levels to those of the excited species
- large molecules with many energy levels

poor collider: *e.g.* noble gases:
no rotational or vibrational energy levels
only the translational mode can be excited

calculation of the effective concentration of M:

m_i: collision efficiency parameter

$$[M] = \sum_i m_{y_i} [Y_i]$$

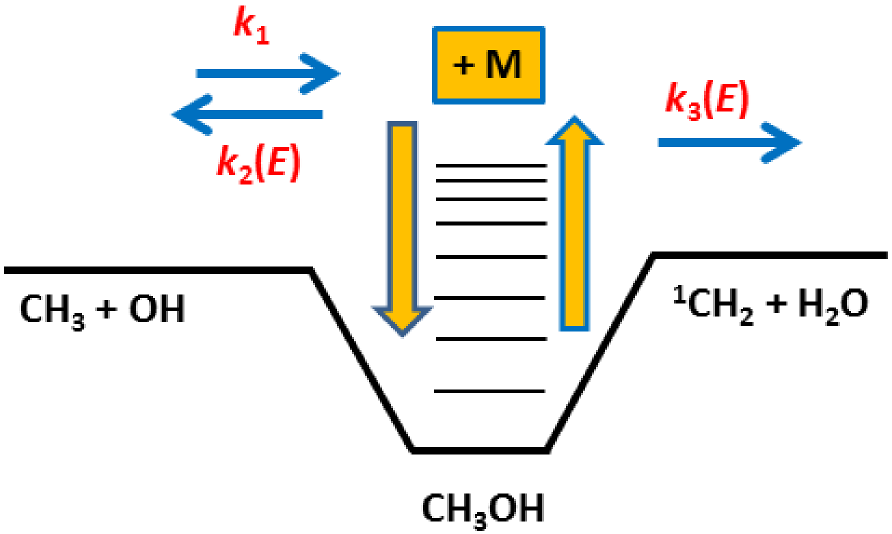
calculation for reaction **H_2O_2 (+M) → .OH + .OH (+M):**

$[M]= 5[H_2O]+5.13[H_2O_2]+0.8[O_2]+2.47[H_2]+1.87[CO]+1.07[CO_2]+0.67[Ar]+0.43[He]+[\text{all others}]$

Pressure dependence of the rate coefficients 2
complex-forming bimolecular reactions

sample reaction: $CH_3 + OH\ (+ M) \rightarrow CH_3OH^* \rightarrow CH_3OH\ (+ M)$

$\rightarrow {}^1CH_2 + H_2O\ (+ M)$



low pressure:

mainly CH_3OH^* decomposition to $^1CH_2 + H_2O$

($^1CH_2$ = singlet CH_2 = electronically excited CH_2)

high pressure:

mainly CH_3OH^* stabilization, giving CH_3OH

$CH_3 + OH \rightarrow CH_3OH$ 3rd order at low pressure, 2nd order at high pressure

$CH_3 + OH \rightarrow {}^1CH_2 + H_2O$ 3rd order at low pressure, 2nd order at high pressure

Formation of the stabilization product

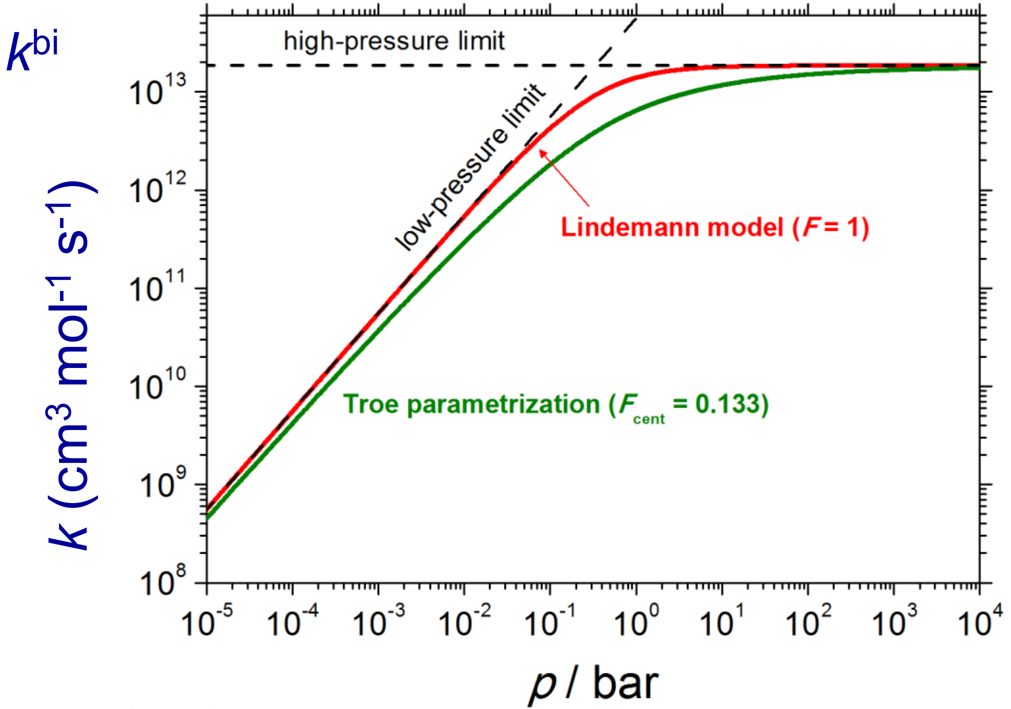
$$k^{\mathrm{bi}} = k_{\infty}\left(\frac{P_r}{1+P_r}\right)F$$

$$P_r = \frac{k_0[\mathrm{M}]}{k_{\infty}}$$

P_r reduced pressure
F controls the shape of the $k(p)$ curve

in the Lindemann model $F = 1$

$CH_3 + OH\ (+\ M) \rightarrow CH_3OH\ (+\ M)$



$F(p,T)$ can be defined by *e.g.* Troe parameterization

k^{bi} „pseudo second order” rate coefficient
at low pressure: $k^{\mathrm{bi}} = k_0\,[\mathrm{M}]$
at high pressure: $k^{\mathrm{bi}} = k_{\infty}$

Formation of the decomposition products

$$k^{\mathrm{tri}} = k_0\left(\frac{1}{1+P_r}\right)F$$

$$P_r = \frac{k_0[\mathrm{M}]}{k_\infty}$$

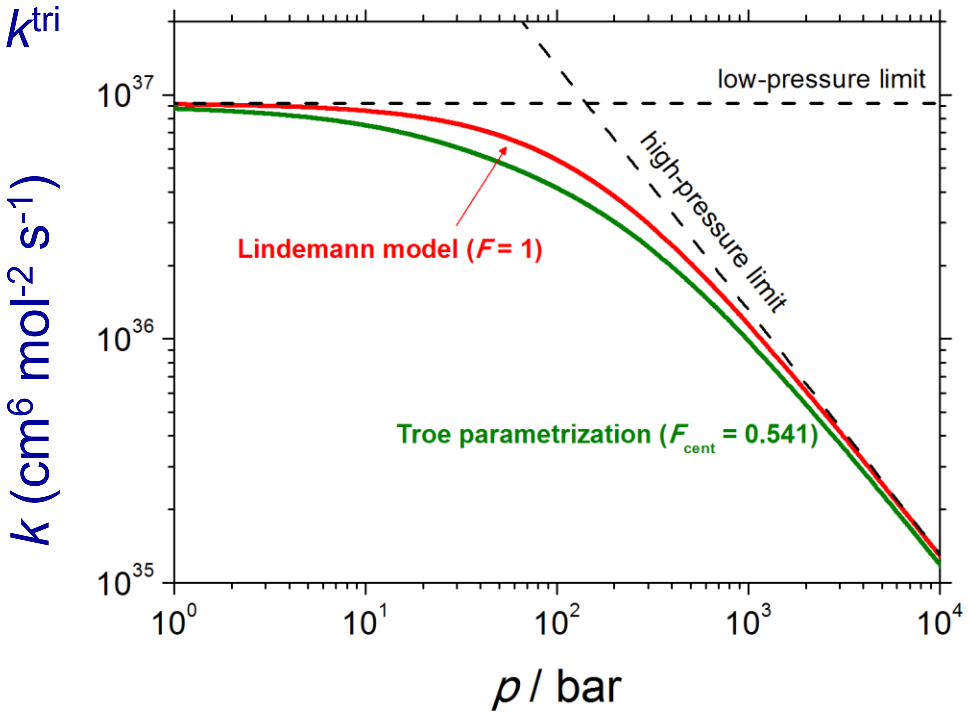
P_r reduced pressure
F controls the shape of the $k(p)$ curve

in the Lindemann model $F = 1$

$F(p,T)$ can be defined by *e.g.* Troe parameterization

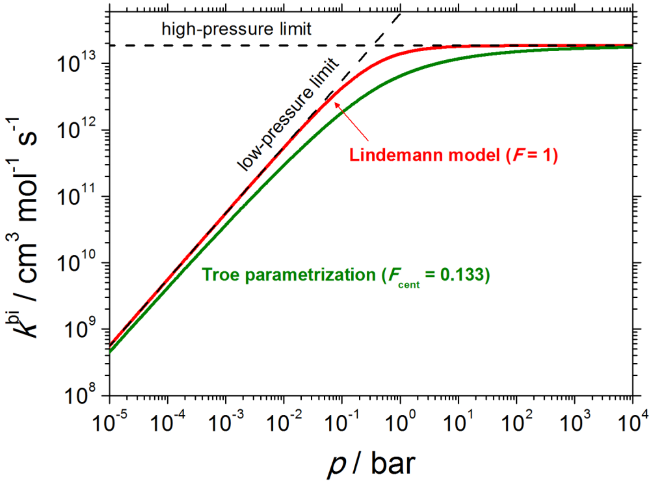
k^{tri} „pseudo third order" rate coefficient
at low pressure: $k^{\mathrm{tri}} = k_0$
at high pressure: $k^{\mathrm{tri}} = k_\infty / [\mathrm{M}]$

$CH_3 + OH\ (+M) \rightarrow {}^1CH_2 + H_2O\ (+M)$

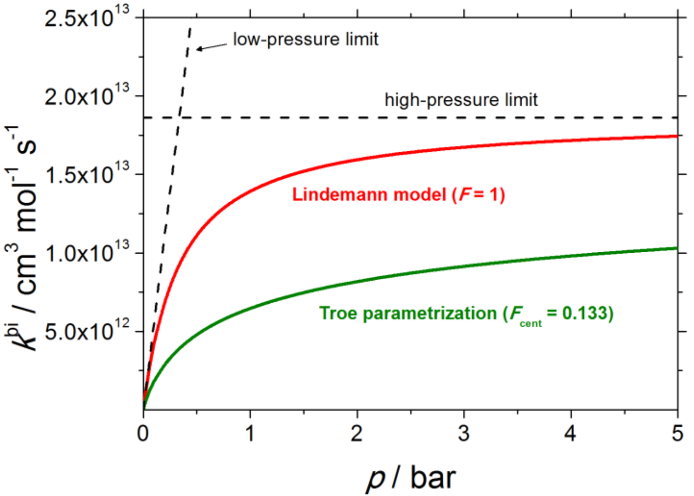


Reaction $CH_3 + OH \rightarrow$ products

$CH_3 + OH\ (+M) \rightarrow CH_3OH\ (+M)$

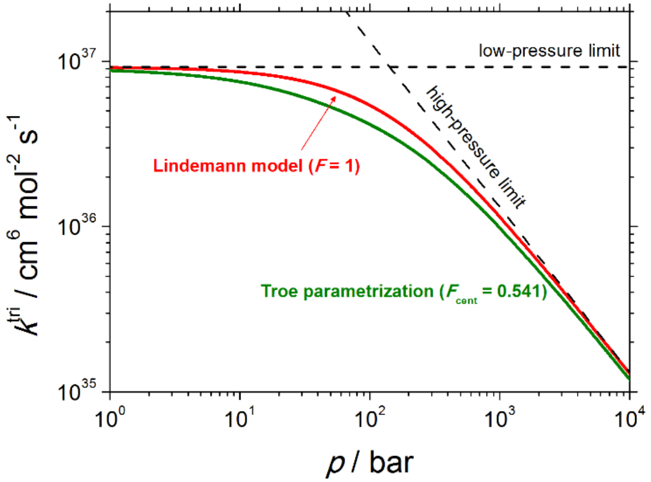


lg k^{bi} – lg p plot

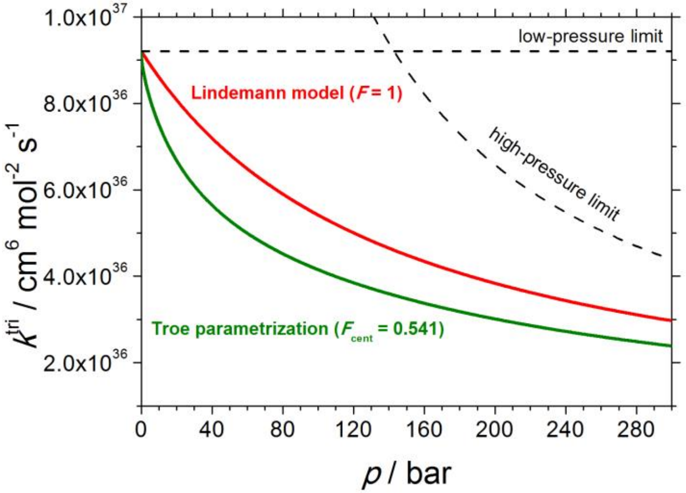


k^{bi} – p plot

$CH_3 + OH\ (+M) \rightarrow {}^1CH_2 + H_2O\ (+M)$



lg k^{tri} – lg p plot



k^{tri} – p plot

T = 1000 K

source of data: R. De Avillez Pereira *et al. J. Phys. Chem. A*, **101**, 9681–9693 (1997)

Simulation of spatially homogeneous systems

calculation of concentration changes
(solution of the kinetic system of differential equations) :

$$\frac{\mathrm{d}\mathbf{Y}}{\mathrm{d}t} = \mathbf{f}\left(\mathbf{Y},\mathbf{p}\right) \qquad \mathbf{Y}(t_0) = \mathbf{Y}_0$$

calculation of temperature changes in an adiabatic system:

rate of reaction step *i*
⇓

$$C_p \frac{\mathrm{d}T}{\mathrm{d}t} = \sum_{i=1}^{N_R} \mathit{\Delta}_r H_i^{\Theta}\, r_i \qquad T(t_0) = T_0$$

heat capacity of the mixture ⇑

⇑ standard reaction enthalpy
of reaction step *i*

CHEMKIN format of mechanisms

```
ELEMENTS  H  O  N  AR  END
SPECIES
H2    O2   H2O   H2O2   H   O   OH   HO2   N2     AR
END
THERMO ALL
   300.000  1000.000  5000.000
H2                  H   2    0    0    0G    300.00   5000.00 1000.00    0 1
 2.99142300E+00 7.00064400E-04-5.63382900E-08-9.23157800E-12 1.58275200E-15    2
-8.35034000E+02-1.35511000E+00 3.29812400E+00 8.24944200E-04-8.14301500E-07    3
-9.47543400E-11 4.13487200E-13-1.01252100E+03-3.29409400E+00                   4
O2                  O   2    0    0    0G    300.00   5000.00 1000.00    0 1
 3.69757800E+00 6.13519700E-04-1.25884200E-07 1.77528100E-11-1.13643500E-15    2
-1.23393000E+03 3.18916600E+00 3.21293600E+00 1.12748600E-03-5.75615000E-07    3
 1.31387700E-09-8.76855400E-13-1.00524900E+03 6.03473800E+00                   4
H2O                 H   2O   1    0    0G    300.00   5000.00 1000.00    0 1
 2.67214600E+00 3.05629300E-03-8.73026000E-07 1.20099600E-10-6.39161800E-15    2
-2.98992                                                                       3
 6.968581
H2O2
 4.573167                                                                      2
-1.80069                                                                       3
-4.62580
H                   H   1    0    0    0G    300.00   5000.00 1000.00    0 1
 2.50000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
 2.54716300E+04-4.60117600E-01 2.50000000E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00 2.54716300E+04-4.60117600E-01                   4
...
```

for each species, the description of the temperature dependence of H, S and c_p
NASA polynomials: 2×7 parameters

CHEMKIN format of mechanisms

```
REACTIONS   MOLES  KJOULES/MOLE
H2+O              => OH+H              5.120E+04   2.67     26.27
OH+H              => H2+O              3.534E+04   2.62     18.95
H2+OH              => H2O+H              1.020E+08   1.60
H2O+H              => H2+OH              4.520E+08   1.60
O2+H+M              => HO2+M               2.100E+18   -.80      .00
 N2/0.67/ O2/0.4/ H2O/0./ AR/0.28/
HO2+M               => O2+H+M              1.159E+20  -1.26    211.41

                                                   .00     -8.73
HO2+H2O              => O2+H+H2O              3.801E+17  -.46    202.68
O2+H              => OH+O              9.756E+13   .00     62.11
OH+O              => O2+H              1.450E+13   .00      2.94
H2O2+O              => OH+HO2              6.620E+11   .00     16.63
OH+HO2              => H2O2+O              4.073E+08   .72     77.51
H2O2+OH              => H2O+HO2              7.830E+12   .00      5.57
H2O+HO2              => H2O2+OH              4.744E+11   .45    140.59
H2O2(+M)             => 2OH(+M)              3.000E+14   .00    202.87
 N2/0.4/ O2/0.4/ H2O/6.5/ AR/0.35/
   LOW /  3.000E+17    .00    190.40 /
   TROE /    1.0000      1.00      1.00   1040.00 /
2OH(+M)              => H2O2(+M)             7.230E+13  -.37      .00
 N2/0.4/ O2/0.4/ H2O/6.5/ AR/0.35/
   LOW /  5.530E+19    .76       .00 /
   TROE /    1.0000      1.00      1.00   1040.00 /
…
…
END
```

Arrhenius parameters *A, n, E*

3rd body collision efficiencies

Arrhenius parameters of k_0

Troe-parameters for the desciption of *p*-dependence

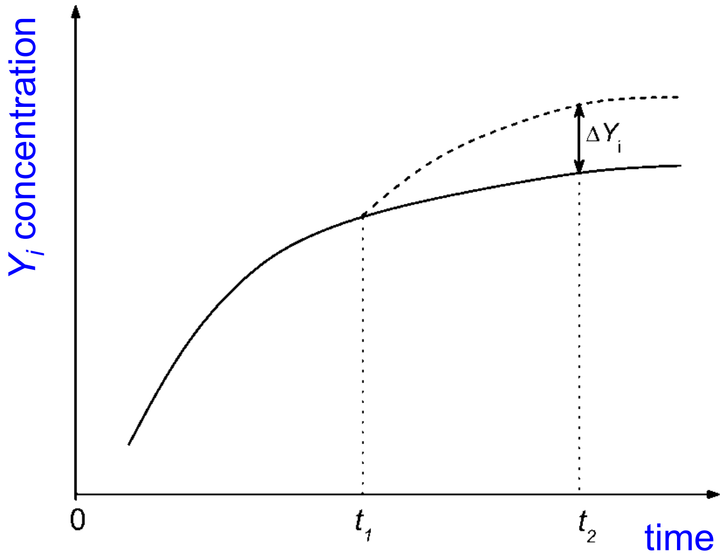
Local sensitivity analysis

Sensitivity analysis is a family of mathematical methods.
It investigates the dependence of the model results
on the values of the parameters

Local sensitivity analysis: investigates the effect of the small change of parameters

Local sensitivity coefficients can be investigated by a
finite difference approximation:

$$\frac{\partial Y_i}{\partial p_j}(t_1,t_2) \approx \frac{\Delta Y_i(t_2)}{\Delta p_j} = \frac{Y_i'(t_2) - Y_i(t_2)}{\Delta p_j}$$



parameter is changed at time t_1
the result is observed at time t_2

T. Turányi: Sensitivity analysis of complex kinetic systems: Tools and applications, *J. Math. Chem.*, **5**, 203-248(1990)

Local sensitivity analysis 2

Another approach: Taylor series expansion

$$Y_i(t,\mathbf{p}+\Delta\mathbf{p}) = Y_i(t,\mathbf{p}) + \sum_{j=1}^{m} \frac{\partial Y_i}{\partial p_j}\Delta p_j + \frac{1}{2}\sum_{k=1}^{m}\sum_{j=1}^{m} \frac{\partial^2 Y_i}{\partial p_k \partial p_j}\Delta p_k \Delta p_j + \ldots$$

Local sensitivity coefficient: $s_{ik} = \frac{\partial Y_i}{\partial p_k}$

Local sensitivity matrix: $\mathbf{S} = \left\{ \frac{\partial Y_i}{\partial p_k} \right\}$

The effect of parameter changes can be estimated using local sensitivities:

Changing a single parameter: $Y_i'(t_2) = Y_i(t_2) + \frac{\partial Y_i}{\partial p_j}\Delta p_j$

Changing several parameters: $\mathbf{Y}'(t_2) = \mathbf{Y}(t_2) + \mathbf{S}(t_1,t_2)\Delta\mathbf{p}(t_1)$

Local sensitivity analysis 3

$$\frac{\mathrm{d}\,\mathbf{Y}}{\mathrm{d}\,t} = \mathbf{f}\left(\mathbf{Y},\mathbf{p}\right) \qquad\qquad \mathbf{Y}(t_0) = \mathbf{Y}_0$$

Differentiation with respect *p*p_j

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\frac{\partial \mathbf{Y}}{\partial p_j} = \mathbf{J}\frac{\partial \mathbf{Y}}{\partial p_j} + \frac{\partial \mathbf{f}}{\partial p_j} \qquad \frac{\partial\,\mathbf{Y}}{\partial\,p_j}\left(t_0\right) = 0 \qquad j = 1,\, 2,\, \ldots,\, m$$

The same equation with matrix-vector notation:

$$\dot{\mathbf{S}} = \underbrace{\mathbf{J}\,\mathbf{S}}_{\text{indirect effect}} + \underbrace{\mathbf{F}}_{\text{direct effect}}, \quad \mathbf{S}\left(0\right) = \mathbf{0}$$

where $\mathbf{J} = \left\{\frac{\partial f_i}{\partial Y_j}\right\}$ $\quad \mathbf{F} = \left\{\frac{\partial f_j}{\partial p_k}\right\}$

Initial concentration sensitivities

initial concentration sensitivities: the consequence of changing the initial conc. can be calculated with finite differences:

$$\frac{\partial Y_i}{\partial Y_j(t_1)}(t_2) \approx \frac{\Delta Y_i(t_2)}{\Delta Y_j(t_1)} = \frac{Y_i'(t_2) - Y_i(t_2)}{\Delta Y_j(t_1)}$$

kinetic system of ODEs: $\frac{\mathrm{d}\mathbf{Y}}{\mathrm{d}t} = \mathbf{f}(\mathbf{Y}, \mathbf{p}) \qquad \mathbf{Y}(t_0) = \mathbf{Y}_0$

Differentiating it with respect to $Y_j(t_1)$:

$$\frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial \mathbf{g}}{Y_j^0(t_1)} = \mathbf{J} \frac{\partial \mathbf{g}}{\partial Y_j^0(t_1)} \qquad \frac{\partial \mathbf{Y}}{\partial Y_j^0(t_1)}(t_1) = \boldsymbol{\delta}_j \qquad j = 1, 2, \ldots, n$$

$$\frac{\mathrm{d}}{\mathrm{d}t} \mathbf{G}(t, t_1) = \frac{\partial \mathbf{f}}{\partial \mathbf{Y}}(t)\, \mathbf{G}(t, t_1) \qquad \mathbf{G}(t_1, t_1) = \mathbf{I}$$

the initial value of variable *j* is changed at time t_1 and
the effect is read at time t_2

$$g_{ij}(t, t_1) = \frac{\partial Y_i(t)}{\partial Y_j^0(t_1)} \qquad \mathbf{g}_j(t, t_1) = \frac{\partial \mathbf{Y}(t)}{\partial Y_j^0(t_1)}$$

Green function matrix **G**

Calculation of local sensitivity coefficients

1 Brute force method (finite difference approximation)

$$\frac{\partial Y_i}{\partial p_j(t_1)}(t_2) \approx \frac{\Delta Y_i(t_2)}{\Delta p_j(t_1)} = \frac{Y_i'(t_2) - Y_i(t_2)}{\Delta p_j(t_1)}$$

Δp_j small: large error due to the representation of numbers

Δp_j large: large error due to nonlinearity

2 Direct method

2a. Coupled Direct Method:

coupled solution of the kinetic and sensitivity differential equations:

$$\frac{\mathrm{d}\,\mathbf{Y}}{\mathrm{d}\,t} = \mathbf{f}(\mathbf{Y}, \mathbf{p}) \qquad \mathbf{Y}(t_0) = \mathbf{Y}_0$$

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\frac{\partial \mathbf{Y}}{\partial p_j} = \mathbf{J}\frac{\partial \mathbf{Y}}{\partial p_j} + \frac{\partial \mathbf{f}}{\partial p_j} \qquad \frac{\partial\,\mathbf{Y}}{\partial\,p_j}(t_0) = 0$$

The coupled solution is repeated for each parameter: $j = 1, 2, \ldots, m$

Lots of unnecessary calculations.

Calculation of local sensitivity coefficients 2

2b. Decoupled Direct Method (DDM):

joint solution of the kinetic and sensitivity diff. equations in each step:

$$\frac{\mathrm{d}\,\mathbf{Y}}{\mathrm{d}\,t}=\mathbf{f}\left(\mathbf{Y},\mathbf{p}\right) \qquad \mathbf{Y}(t_0)=\mathbf{Y}_0$$

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\frac{\partial \mathbf{Y}}{\partial p_j}=\mathbf{J}\frac{\partial \mathbf{Y}}{\partial p_j}+\frac{\partial \mathbf{f}}{\partial p_j} \qquad \frac{\partial\,\mathbf{Y}}{\partial\,p_j}\left(t_0\right)=0 \qquad j=1,\,2,\,\ldots,\,m$$

The Jacobian of these equations are identical, therefore in each step

⇒ transformation of the Jacobian to a triangle matrix

⇒ selection of stepsize Δt based on the Jacobian

⇒ solution of the stiff ODE: calculation of new **Y**

⇒ calculation of the new sensitivity vector for parameter j =1
using the same triangle matrix

⇒ ⇒ ⇒ ⇒ ⇒ repeating for all parameters $j=1,\,2,\,\ldots,\,m$

⇒ ⇒ repeating for new time steps from the transformation of **J**

features:

- very fast method; the computer time only slightly increases with the number of parameters m (because the transformation of **J** is the most time-consuming)
- the accuracy of the solution can be controlled

Interpretation of local sensitivity coefficients

$$s_{ik} = \frac{\partial Y_i}{\partial p_k}$$

(Original) local sensitivity coefficients:
the parameter is changed by one unit
inspected: the result is changed by how many units
[unit of result / unit of parameter]

Normalized local sensitivity coefficients:

$$\tilde{s}_{ik} = \frac{p_k}{Y_i}\frac{\partial Y_i}{\partial p_k} = \frac{\partial \ln Y_i}{\partial \ln p_k}$$

investigates relative changes
How much % change of the result
due to 1 % change of the parameter?
dimension free

So far: single parameter is changed
effect on a single model result is investigated

Further information can also be extracted from sensitivity matrix **S** using principal component analyis, like the case when
several parameters are changed simultaneously, and
the effect on multiple model results is investigated.

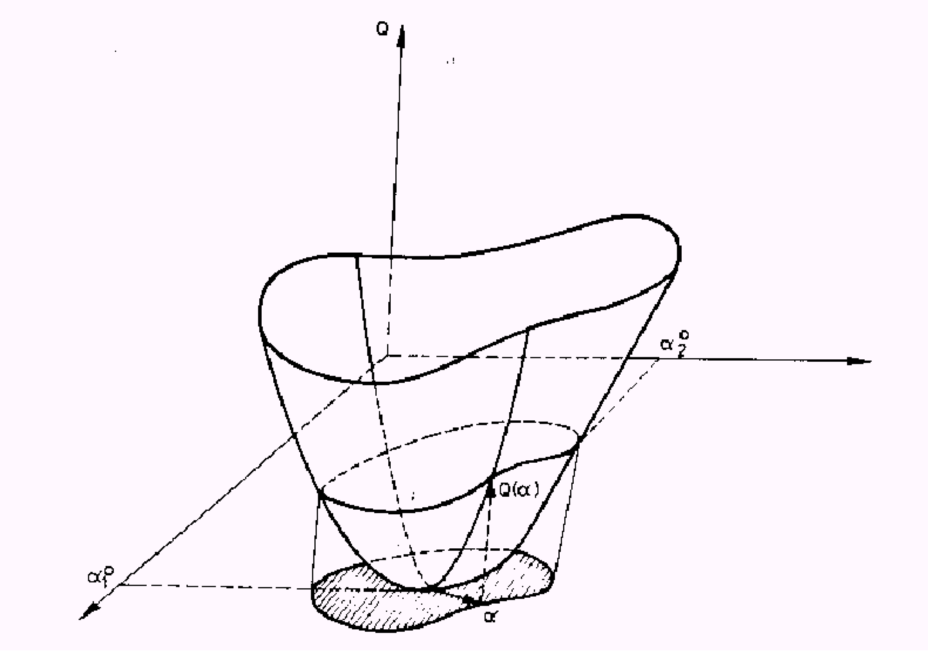
PCAS: principal component analysis of the sensitivity matrix S

Several parameters are changed simultaneously and the effect on several model outputs is investigated.

The effect of changing parameters is measured by a

Célfüggvény:

$$e(\mathbf{p}) = \int_{t_1}^{t_2} \sum_{i=1}^{m} \left(\frac{Y_i^*(t) - Y_i(t)}{Y_i(t)} \right)^2 \mathrm{d}t$$

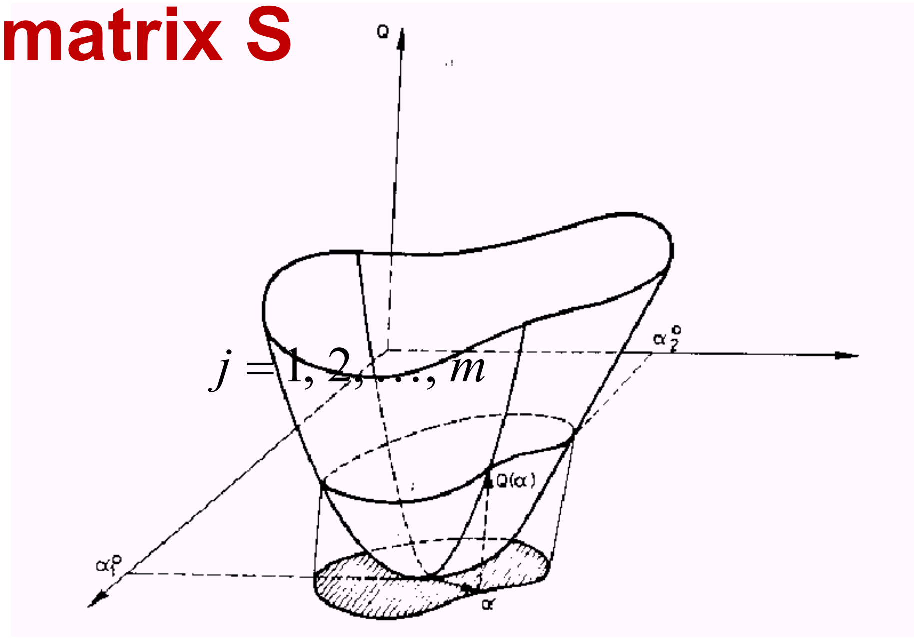


S. Vajda, P. Valkó, T. Turányi: Principal component analysis of kinetic models
Int. J. Chem. Kinet., **17**, 55-81(1985)

PCAS: principal component analysis of the sensitivity matrix S

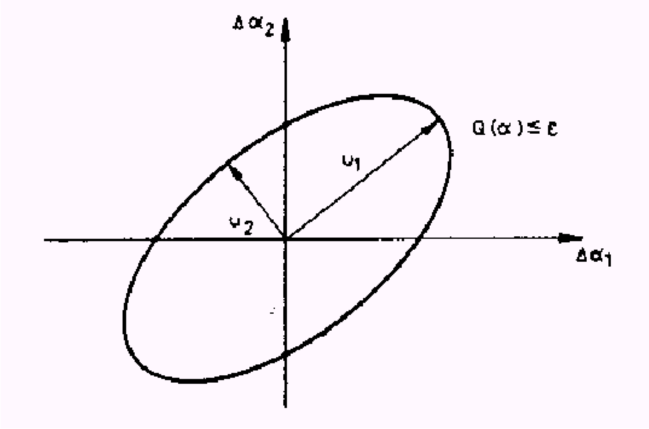
The objective function can be approximated by:

$$e(\boldsymbol{\alpha}) = (\Delta\boldsymbol{\alpha})^{\mathrm{T}}\widetilde{\mathbf{S}}^{\mathrm{T}}\widetilde{\mathbf{S}}(\Delta\boldsymbol{\alpha})$$



where

$$\Delta\boldsymbol{\alpha} = \Delta \ln \mathbf{p} \qquad \widetilde{\mathbf{S}} = \begin{bmatrix} \widetilde{\mathbf{S}}_1 \\ \widetilde{\mathbf{S}}_2 \\ \vdots \\ \widetilde{\mathbf{S}}_n \end{bmatrix}$$

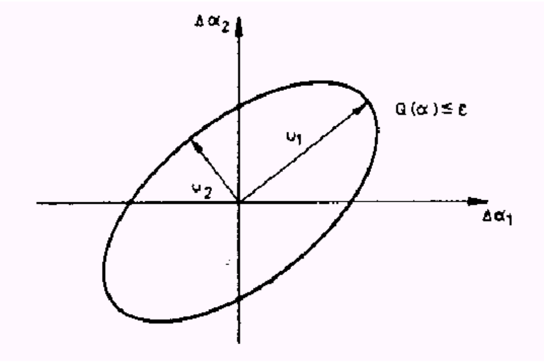


And the normed sensitivity matrix belonging to time t_r

$$\widetilde{\mathbf{S}}_r = \{(p_k / Y_i)(\partial Y_i(t_r) / \partial p_k)\}$$

PCAS: principal component analysis of the sensitivity matrix S

$$e(\boldsymbol{\alpha}) = (\Delta\boldsymbol{\alpha})^{\mathrm{T}} \widetilde{\mathbf{S}}^{\mathrm{T}} \widetilde{\mathbf{S}} (\Delta\boldsymbol{\alpha})$$



This quadratic form determines a (hyper) ellipsoid:

2D ellipse
3D ellipsoid (rugby ball shape)
4D hyper ellipsoid

Another characterization of the hyper ellipsoid:
- lengths of the axes
- directions of the axes

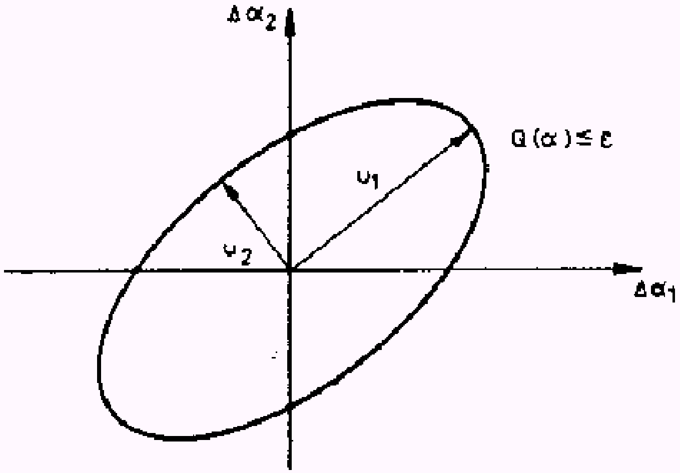
Eigenvalue-eigenvector decomposition of matrix $\widetilde{\mathbf{S}}^{\mathrm{T}} \widetilde{\mathbf{S}}$

λ_i eigenvalue *i* = length of axis *i*
if λ_i is small: the objective function increases rapidly to this direction
= parameter group *i* is highly influental

$\mathbf{u}_i$ eigenvector *i* = direction of axis *i*

PCAS: principal component analysis of the sensitivity matrix S

$$e(\boldsymbol{\alpha}) = (\Delta\boldsymbol{\alpha})^{\mathrm{T}} \widetilde{\mathbf{S}}^{\mathrm{T}} \widetilde{\mathbf{S}} (\Delta\boldsymbol{\alpha})$$



An alternative form of the objective function:

$$e(\boldsymbol{\alpha}) = \sum_{i=1}^{r} \lambda_i (\Delta\Psi_i)^2$$

where $\Delta\Psi_i = \mathbf{u}_i \boldsymbol{\alpha}$ transformed parameters called principal components

In the figure above:

λ_1 small ⇒ axis 1 is long; $\mathbf{u}_1 = (0.707, 0.707)$

λ_2 large ⇒ axis 2 is short; $\mathbf{u}_2 = (-0.707, 0.707)$

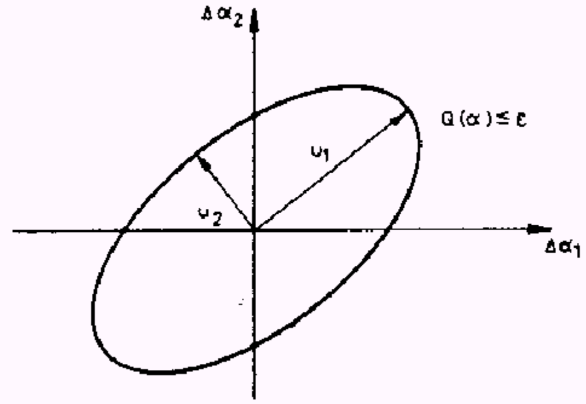
Note: the eigenvectors are unit vectors, therefore $0{,}707^2+0{,}707^2= 1$

PCAS: principal component analysis of the sensitivity matrix S

Example 1:

λ_1 small $\Rightarrow$ axis 1 is long; $\mathbf{u}_1 = (0.707, 0.707)$

λ_2 large $\Rightarrow$ axis 2 is short; $\mathbf{u}_2 = (-0.707, 0.707)$



axis 1 is long → changing the parameters to direction $\mathbf{u}_1$
the objective function changes little

→ if $\alpha_2 - \alpha_1 = \ln p_2 - \ln p_1 = \ln (p_2/p_1)$ constant, $\Rightarrow$ little change of the objective function

→ if p_2/p_1 constant, $\Rightarrow$ little change of the objective function

Thus, eigenvector $\mathbf{u} = (0.707, 0.707)$ means that keeping the ratio of the corresponding two parameters constant the inspected result(s) of simulation do not change.

Chemistry: the model results do not change if we keep the equilibrium constant $K = k_1/k_2$ fixed.

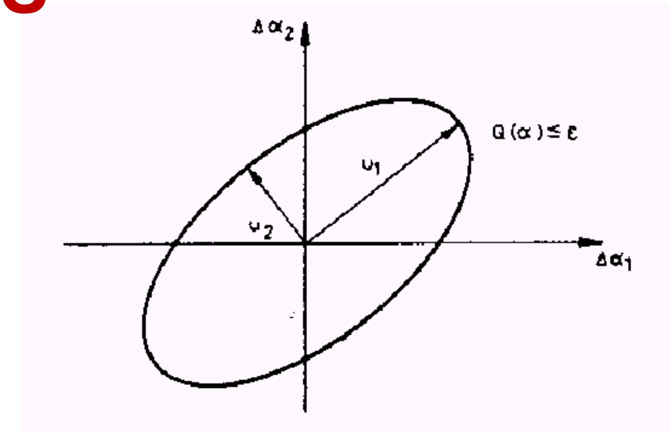
PCAS: principal component analysis of the sensitivity matrix S

Example 2:

$\mathbf{u}_1$ = (0.707, 0.707, 0) large eigenvalue

$\mathbf{u}_2$ = (-0.707, 0.707, 0) small eigenvalue

$\mathbf{u}_3$ = (0 , 0 , 1) large eigenvalue



Interpretation of the eigenvectors:

p_1/p_2 and p_3 can be determined from the experimental data

p_3 can be determined independently

Only the ratio of p_1 and p_2 can be determined.

T. Perger, T. Kovács, T. Turányi, C. Treviño:
Determination of adsorption and desorption parameters from ignition temperature measurements in catalytic combustion systems, *J. Phys. Chem. B*, **107**, 2262-2274 (2003)

Local uncertainty analysis

If the parameters are correlated, then using the rule of spread of errors
the uncertainty of model results
can be calculated from the correlation matrix of parameters:

$$\boldsymbol{\sigma}_{\mathbf{Y}} = \mathbf{S}^{\mathrm{T}} \boldsymbol{\Sigma}_p \mathbf{S}$$

Here $\Sigma_{\mathbf{p}}$ is the covariance matrix of parameters, **S** is the sensitivity matrix and $\boldsymbol{\sigma}_{\mathrm{Y}}$ is the variance of simulation results.

If the parameters are uncorrelated, then variance $\sigma^2(y)$ of model result *y*

can be calculated from the variance of parameters: $\sigma^2(p_k)$

$\sigma_k^2(y)$ is the contribution of parameter *k* to the variance of model result *y*

$$\sigma_k^2(y) = \sigma^2(p_k)\left(\frac{\partial y}{\partial p_k}\right)^2 \qquad \sigma^2(y) = \sum_k \sigma_k^2(y)$$

Local uncertainty analysis of chemical kinetic models

$f_j \rightarrow \sigma^2(\ln k_j)$ uncertainty parameter f_i is transformed to the variance of ln k_j

$\partial Y_i / \partial \ln k_j$ seminormalized local sensitivity coefficients

$$\sigma^2_{\mathrm{K}\,j}(Y_i) = \left(\partial Y_i / \partial \ln k_j\right)^2 \sigma^2(\ln k_j)$$

contribution of the uncertainty of parameter k_{j} to the variance of result Y_{i}

$\sigma^2_{\mathrm{K}}(Y_i) = \sum_j \sigma^2_{\mathrm{K}\,j}(Y_i)$ variance of result Y_{i} due to kinetic uncertainties

$$\sigma^2_{T\,j}(Y_i) = \left(\partial Y_i / \partial \Delta_f H^{\circ}_{298}(j)\right)^2 \sigma^2\left(\Delta_f H^{\circ}_{298}(j)\right)$$

contribution of the uncertainty of the enthalpy of formation of species *j* to the variance of result Y_{i}

$$\sigma^2(Y_i) = \sigma^2_K(Y_i) + \sigma^2_T(Y_i) = \sum_j \sigma^2_{K\,j}(Y_i) + \sum_j \sigma^2_{T\,j}(Y_i)$$

estimated total variance of result Y_{i} from both kinetic and thermodynamic uncertainties

T. Turányi, L. Zalotai, S. Dóbé, T. Bérces:
Effect of the uncertainty of kinetic and thermodynamic data on
methane flame simulation results, *Phys.Chem.Chem.Phys.*, **4**, 2568-2578 (2002)

Local uncertainty analysis 3

- Linear approximation of the variance of the model result
- Does not take into account the nonlinear effects
- The result belongs to the nominal set of model parameters
- Realistic results, if the model behaves qualitatively similarly in the whole domain of parameters
- Non-realistic results, if the model is qualitatively different in the various parts of the parameter domain
- Provides separately the contribution of parameters
- Can be calculated fast

Applications of local sensitivities

1. Analysis of models
   - Estimation of the effect of parameter perturbation
   - Identification of cooperating parameters
2. Reduction of models
   - Identification of ineffective parameters; production of a simpler model with less parameters, but almost identical results
3. Local uncertainty analysis
   - May replace global uncertainty analysis: less accurate, much faster
4. Parameter estimation / model optimization
   - All gradient methods are based on the (hidden) application of local sensitivity coefficients
   - Identification of effective parameters
   - Experimental design

Thank you for your attention!