Lecture 2

Reaction kinetics simulations, sensitivity and uncertainty analyses

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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

$2\ H_2 + O_2 = 2\ H_2O$

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

$$0 = \sum_j \nu_j A_j$$

$\nu_1 = -2$ A_1 = „H_2”

$\nu_2 = -1$ A_2 = „O_2”

$\nu_3 = +2$ 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: $\mathbf{J} = \left\{ \dfrac{\partial f_i}{\partial y_j} \right\}$

The Jacobian usually changes with changing concentrations

matrix F: $\mathbf{F} = \left\{ \dfrac{\partial f_i}{\partial k_j} \right\}$

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.	$X + Z \rightarrow 0.5\,X + A$	k_5	$r_5 = k_5xz$
6.	$Z + M \rightarrow Y - Z$	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.	$Z + M \rightarrow Y - Z$

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

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

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

calculation of the Jacobian

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

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

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

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

$\frac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial x} = -k_1y - 4k_3x + k_4a - 0{,}5k_5z$	$\frac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial y} = -k_1x + k_2a$	$\frac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial z} = -0.5k_5x$
$\frac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial x} = -k_1y$	$\frac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial y} = -k_1x - k_2a$	$\frac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial z} = +k_6m$
$\frac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial x} = 2k_4a - k_5z$	$\frac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial y} = 0$	$\frac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial z} = -k_5x - 2k_6m$

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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 (d*c* / d*t*), 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

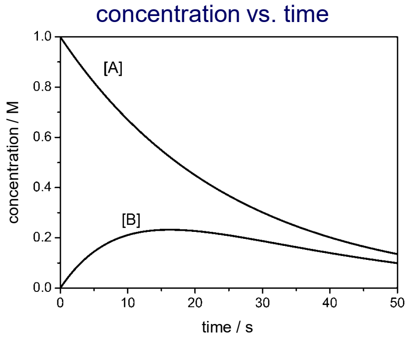
Trajectory

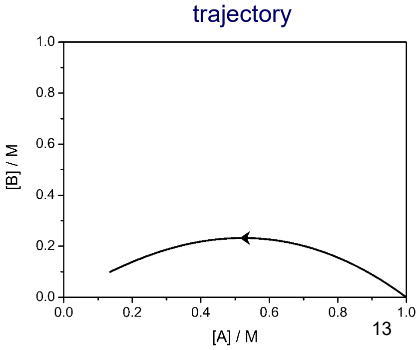
Actual state of the system: a point in the phase space

History of events: trace of this point in the phase space (a solid line)

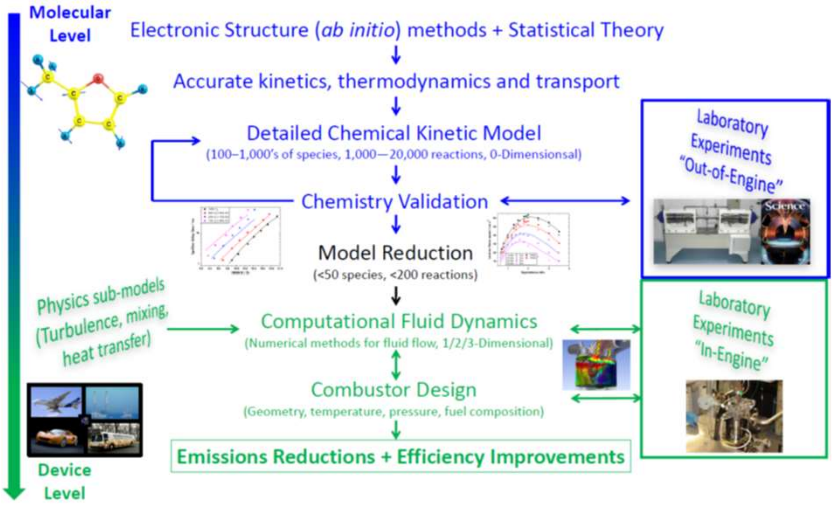
In chemical kinetics this phase space can be the space of concentrations. This figure does not show time, but can be more intersting than the usual concentration vs. time curces.

Example: reaction A → B →





Hierarchy of combustion models



Electronic Structure (*ab initio*) methods + Statistical Theory

Accurate kinetics, thermodynamics and transport

Detailed Chemical Kinetic Model
(100–1,000's of species, 1,000—20,000 reactions, 0-Dimensionsal)

Chemistry Validation

Model Reduction
(<50 species, <200 reactions)

Physics sub-models (Turbulence, mixing, heat transfer)

Computational Fluid Dynamics
(Numerical methods for fluid flow, 1/2/3-Dimensional)

Combustor Design
(Geometry, temperature, pressure, fuel composition)

Emissions Reductions + Efficiency Improvements

Henry J. Curran: Developing detailed chemical kinetic mechanisms for fuel combustion
Proc.Combust.Inst., **37**, 57-81 (2019)

Source of chemical kinetic data

measured and calculated chemical kinetic data → journal publications

data compilation → books. data bases.
e.g. **NIST database**
www.nist.gov

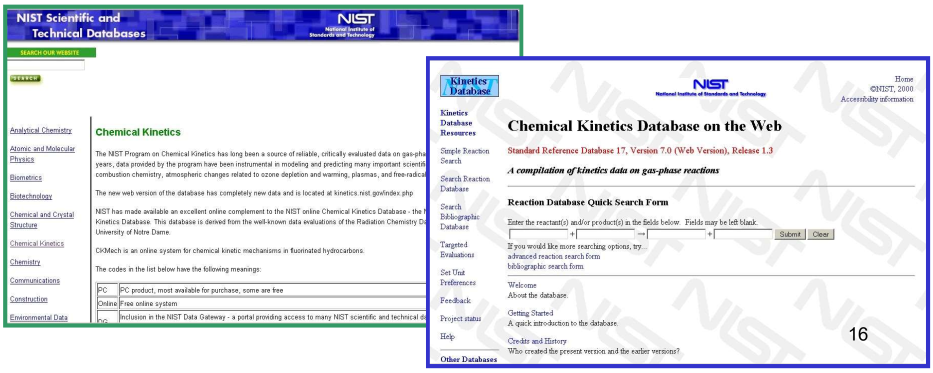
data evaluation → review articles
reevaluation and comparison of several articles
evaluated/recommended data

NIST Chemical Kinetics Database

www.nist.gov

⇒ Databases ⇒ Chemical Kinetics
⇒ NIST Chemical Kinetics Online (http://kinetics.nist.gov/kinetics/)

NIST Chemical Kinetics Database	11.700 gas phase reactions 38.000 data entry 12.000 referenced articles



Chemical Kinetics

The NIST Program on Chemical Kinetics has long been a source of reliable, critically evaluated data on gas-pha
years, data provided by the program have been instrumental in modeling and predicting many important scientifi
combustion chemistry, atmospheric changes related to ozone depletion and warming, plasmas, and free-radical

The new web version of the database has completely new data and is located at kinetics.nist.gov/index.php

NIST has made available an excellent online complement to the NIST online Chemical Kinetics Database - the N
Kinetics Database. This database is derived from the well-known data evaluations of the Radiation Chemistry Da
University of Notre Dame.

CKMech is an online system for chemical kinetic mechanisms in fluorinated hydrocarbons.

The codes in the list below have the following meanings:

PC	PC product, most available for purchase, some are free
Online	Free online system
DG	Inclusion in the NIST Data Gateway - a portal providing access to many NIST scientific and technical da

Chemical Kinetics Database on the Web

Standard Reference Database 17, Version 7.0 (Web Version), Release 1.3

A compilation of kinetics data on gas-phase reactions

Reaction Database Quick Search Form

Enter the reactant(s) and/or product(s) in the fields below. Fields may be left blank.

☐ + ☐ → ☐ + ☐

If you would like more searching options, try...
advanced reaction search form
bibliographic search form

Welcome
About the database.

Getting Started
A quick introduction to the database.

Credits and History
Who created the present version and the earlier versions?

NIST Chemical Kinetics Database 2

Author(s): Gierczak. T.; Talukdar. R.K.; Herndon. S.C.; Vaghjiani. G.L. Ravishankara. A.R.

Title: Rate coefficients for the reactions of hydroxyl radicals with methane and deuterated methanes
Journal: J. Phys. Chem. A:
Volume: 101
Page(s): 3125 - 3134
Year: 1997
Reference type: Journal article
Squib: 1997GIE/TAL3125-3134

Reaction: $CH_4 + \cdot OH \rightarrow \cdot CH_3 + H_2O$
Reaction order: 2
Temperature: 196 - 420 K
Pressure: 0.13 Bar
Rate expression: 1.76×10^{-13} (cm^3/molecule s) $(T/298\ K)^{2.82}\ e^{-1.96\ (\pm 0.02\ kcal/mole)/RT}$
Bath gas: He
Data type: Absolute value measured directly
Excitation technique: Flash photolysis (laser or conventional)
Analytical technique: Laser induced fluorescence

NIST Chemistry WebBook

Another important Web source:
Webbook (http://webbook.nist.gov/)

- thermochemical data for over 7000 compounds
- reaction thermochemistry data for over 8000 reactions.
- IR spectra for over 16.000 compounds.
- mass spectra for over 33.000 compounds.
- UV/Vis spectra for over 1600 compounds.
- gas chromatography data for over 27.000 compounds.
- electronic and vibrational spectra for over 5000 compounds.
- spectroscopic data for over 600 compounds.
- ion energetics data for over 16.000 compounds.
- thermophysical property data for 74 fluids.

Traditional way for the development of detailed reaction mechanisms

1. List of elementary reactions is generated
2. Determination of the rate parameters one-by-one:

   Based on direct measurements
   Using chemical kinetic databases
   Calculation/estimation of rate parameters

3. Comparison of the simulation results with the results of indirect measurements.

   Indirect measurements: time-to-ignition, flame velocity, concentration–time or concentration–distance profiles.

   No good agreement in most cases

4. Identification of the most important reactions by sensitivity analysis at the experimental conditions.
5. Tuning the rate parameters of the most important reactions, till the model reproduces the experimental data.

   Different authors tune different parameters
   ⇒ different mechanisms

Local sensitivity analysis

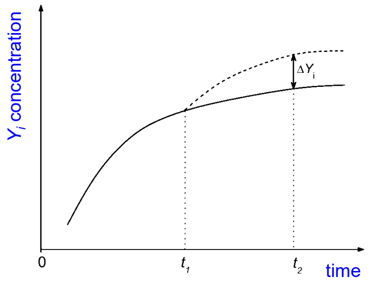
Sensitivity analysis is a family of mathematical methods.
It investigates the dependence of the model results on the values of the parameters

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

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

Differentiation with respect *p_j*

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

The same equation with matrix-vector notation:

$$\dot{\mathbf{S}} = \underbrace{\mathbf{J}\,\mathbf{S}}_{\text{indirect effect}} + \underbrace{\mathbf{F}}_{\text{direct effect}}, \quad \mathbf{S}(0) = \mathbf{0} \qquad \text{where} \quad \mathbf{J} = \left\{\frac{\partial f_i}{\partial Y_j}\right\} \qquad \mathbf{F} = \left\{\frac{\partial f_j}{\partial p_k}\right\}$$

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

coupled solution of the kinetic and sensitivity differential equations:

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

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

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

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:

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

Here $\Sigma_{\mathbf{p}}$ is the covariance matrix of parameters, **S** is the sensitivity matrix and $\Sigma_{\mathbf{Y}}$ is the covariance matrix 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

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 σ_{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*

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

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 2

- 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
   - All gradient methods are based on the (hidden) application of local sensitivity coefficients
   - Identification of effective parameters
   - Experimental design

Global uncertainty analysis

Local uncertainty analysis

Provides information at the nominal parameter set

- well applicable, if the model behaves qualitatively similarly in the various regions of parameter space
- exact for linear models

Global uncertainty analysis

the whole physically possible region of parameters is investigated

Global *vs.* local uncertainty analysis

global methods require much more computer time

acquired information ~ computer time

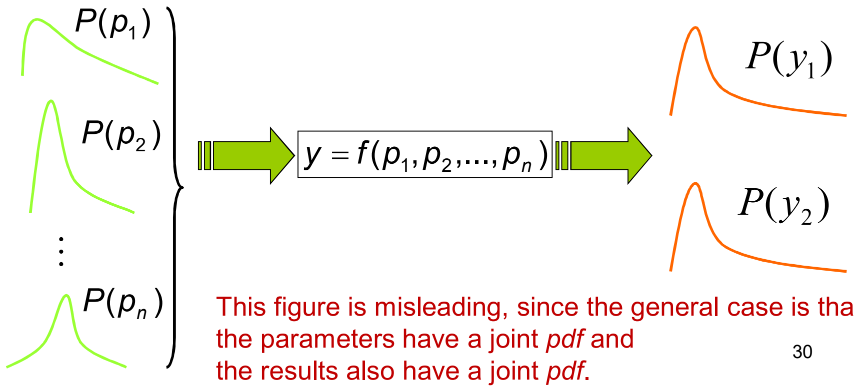
global uncertainty analysis	calculation of the uncertainty of model results from the uncertainty of model parameters
global sensitivity analysis	**as above** + identification of the individual contribution of the uncertainty of model parameters

Global uncertainty analysis 2

The uncertainty of parameters can be characterized by their probability density function (*pdf*)

The aims of global uncertainty analysis:

1. Calculation of the *pdf* of the results on the basis of the *pdf* of parameters
2. Determination of the contribution of the individual parameters to the standard deviation of model results

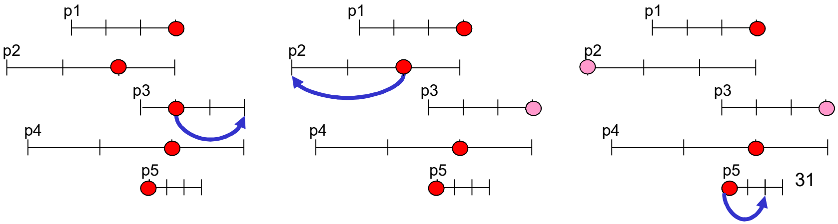


This figure is misleading, since the general case is that the parameters have a joint *pdf* and the results also have a joint *pdf*.

Morris method

Screening methods provide approximate information quickly
The Morris method allows the investigation of the effect of large parameter changes

- lower and upper uncertainty limits are assigned to each parameter.
- the uncertainty interval is divided to *n* parts for each parameter
- random parameter set is selected
- one parameter is changed at each run
- statistical interpretation of the results
- assumes uniform distribution of the parameters
- does not provide the *pdf* of the results
- intermediate computer time

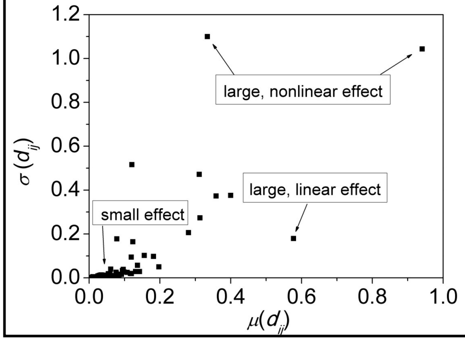


Morris method 2

Value d_{ij} shows the influence of parameter p_j at the random values of all other parameters within their uncertainty interval:

$$d_{ij} = \frac{Y_i\left(p_1^z, p_2^z, \ldots, p_j^z + \Delta, \ldots, p_N^z\right) - Y_i\left(\mathbf{p}^{z-1}\right)}{|\Delta|}$$

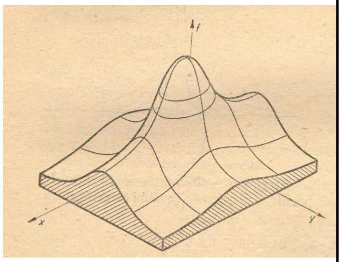
The d_{ij} values are calculated many times in a random calculation and the expected value and standard deviation of d_{ij} is determined.



M. D. Morris:
Factorial sampling plans for preliminary computational experiments.
Technometrics **33**, 161-174 (1991)

F. Campolongo, J. Cariboni, A. Saltelli:
An effective screening design for sensitivity analysis of large models.
Env.Model. Softw. **22**, 1509-1518 (2007)

Monte Carlo method



Several thousands of random parameter sets are generated in accordance with the joint *pdf* of the parameters.

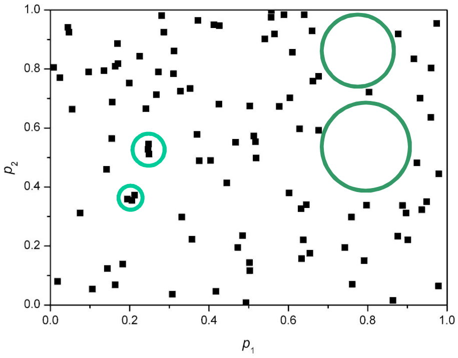
The simulations are carried out at these parameter sets.

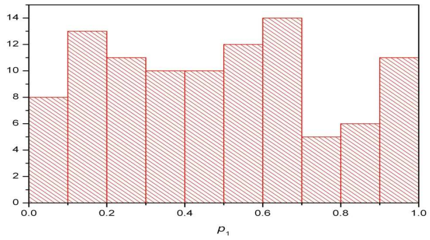
Statistical analysis of the simulation results:
- determination of the histogram of a result
- calculation of the expected value and standard deviation

Problems:
- requires much computer time
- it is not easy to trace the effect of individual parameters

---

Monte Carlo method 2



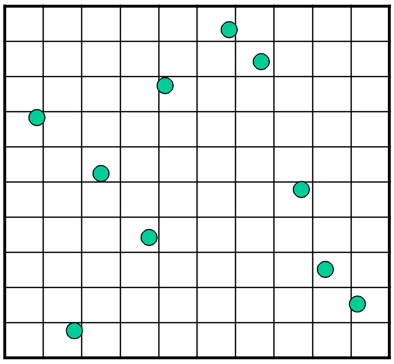


histogram of p_1

Generation of 100 ($\xi.\gamma$) points ξ and γ are random numbers with [0.1] even distribution $\Rightarrow$ used for the generation of parameter values p_1 and p_2 , respectively.

Clogging and empty spots

Monte Carlo method with Latin hypercube sampling



even distribution

M. D. McKay, R. J. Beckman, W. J. Conover: A comparison of three methods for selecting values of input variables in the analysis of output from a computer code. *Technometrics* **42**, 55-61 (2000)

J. C. Helton, F. J. Davis: Latin hypercube sampling and the propagation of uncertainty in analyses of complex systems. *Reliab. Engng Syst. Safety* **81**, 23–69 (2003)

- stripes („*strata*") with equal probability are designated
- within each stripe a point is placed randomly
- if a stripe already contains a point, another point is not placed there

Monte Carlo method with Latin hypercube sampling

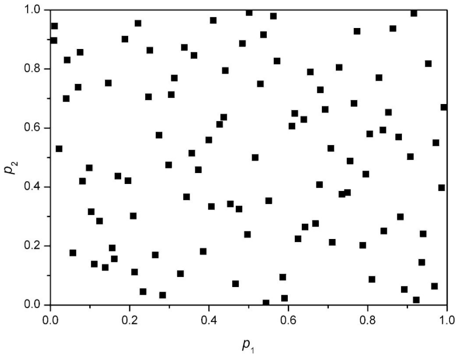
Sir Ronald Aylmer Fisher
(17 February 1890 – 29 July 1962)
British statistician and geneticist.

He has been described as
"a genius who almost single-handedly created the foundations for modern statistical science„.

His contributions to statistics include the maximum likelihood, the derivation of various sampling distributions, founding principles of the design of experiments, and much more. He developed the analysis of variance (ANOVA) method.

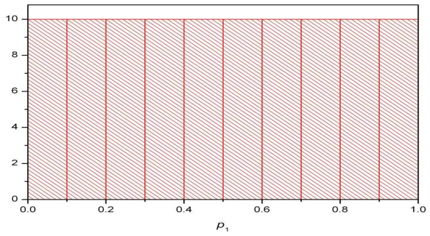
Stained glass window in the dining hall of Caius College, in Cambridge, commemorating Ronald Fisher and representing a Latin square, discussed by him in *The Design of Experiments*

Monte Carlo method with Latin hypercube sampling



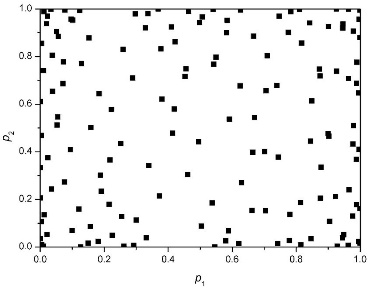
Generation of 100 (ξ.γ) points with Latin hypercube sampling

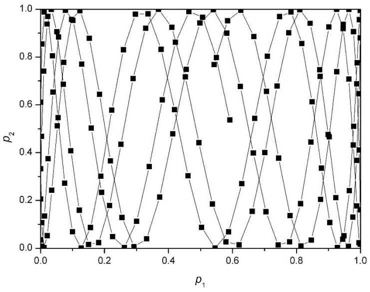
The distribution is much more even



histogram of p_1

Fourier Amplitude Sensitivity Test (FAST) method



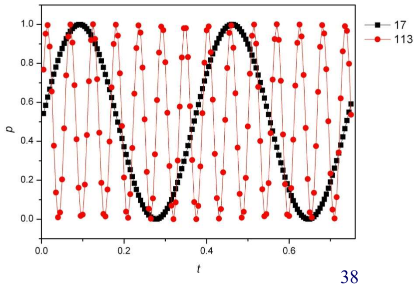


Changing *s* changing the values of sin functions having incommensurable frequency.

The plotted numerical example shows 150 points and $\Delta s = 0.1$

$\mathbf{x} = 0{,}5\ (\sin(17s), \sin(113s)) + 0{,}5$

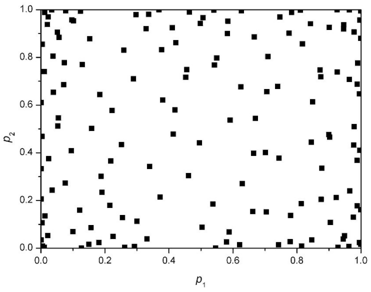
=> scaled to a unit square

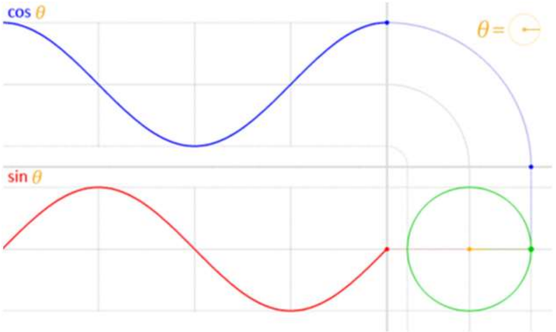


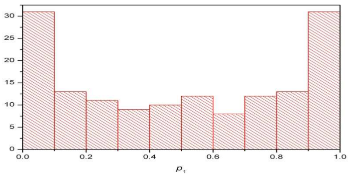
Fourier Amplitude Sensitivity Test (FAST) method 2

If the G_j functions are linear, then
(due to the nature of the sine function)
there are more points at the edges

Using appropriate G_j functions,
an *pdf* can be reconstructed
(for independent parameters)







Fourier Amplitude Sensitivity Test (FAST) method 4

The simulation results are investigated by Fourier analysis:

$$\sigma^2(Y_i) = 2\sum_{l=1}^{+\infty}\left(A_{il}^2 + B_{il}^2\right)$$

Here $\sigma^2(Y_\mathrm{i})$ is the variance of the result; A_il and B_il are the Fourier coefficients:

$$A_{il} = \frac{1}{2\pi}\int_{-\pi}^{\pi} Y_i(s)\cos(ls)\,\mathrm{d}\,s, \quad l = 0, 1, \ldots$$

$$B_{il} = \frac{1}{2\pi}\int_{-\pi}^{\pi} Y_i(s)\sin(ls)\,\mathrm{d}\,s, \quad l = 1, 2, \ldots$$

When the Fourier coefficients are calculated at frequency ω_j and its overtones, then the partial variance caused by parameter *j* is obtained:

$$\sigma_j^2(Y_i) = 2\sum_{r=1}^{+\infty}\left(A_{i,r\omega_j}^2 + B_{i,r\omega_j}^2\right)$$

Fourier Amplitude Sensitivity Test (FAST) method 5

partial variance:

$$S_{ij} = \frac{\sigma_j^2(Y_i)}{\sigma^2(Y_i)}$$

This is the fraction of the total variance caused by parameter *j*

FAST is a slow algorithm; the total number of required simulations:
$N = 1.2\ k^{2,5}$

$N = 21000$ simulations are needed for the investigation of a model having $k = 50$ parameters

The source of extra information for the same amount of computer time:
Unlike in the MC method, the order of simulations is important;
patterns are identified in the sequence of simulations

A. Saltelli, R. Bolado: An alternative way to compute Fourier Amplitude Sensitivity Test (FAST) *Comput. Stat. Data Anal.* **26**, 445-460 (1998)

HDMR method

High Dimensional Model Representation

The simulation results are approximated by a polynomial of the parameters:

$$Y(\mathbf{x}) = Y_0 + \sum_{i=1}^{n} Y_i(x_i) + \sum_{1 \le i < j \le n} Y_{ij}(x_i, x_j) + \dots$$

$Y(x_i)$ the only variable is parameter x_i
But the function can be even an 8th order polynomial!

$Y(x_i, x_j)$ the variables are parameters x_i and x_j
Two variables only, but it can also be a high-order polynomial!

T. Ziehn, A. S. Tomlin: GUI-HDMR - A software tool for global sensitivity analysis of complex models. *Environ. Model. Soft.* **24**, 775-785 (2009)

GUI-HDMR can be downloaded from website https://ReSpecTh.hu

HDMR-method 2

random sampling HDMR (RS-HDMR):
Generation of random points in a parameter domain,
fitting polynomials to these points

Approximation with base functions: $Y_i(x_i)=\sum_{r=1}^{k}\alpha_r^i\,\varphi_r(x_i)$

Partial variances: $D_i=\sum_{r=1}^{k_i}\left(\alpha_r^i\right)^2$

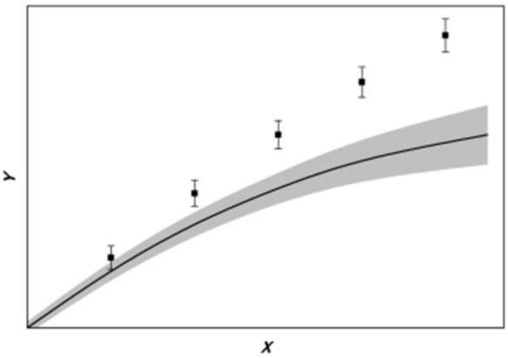
Sensitivity indices: $S_{i_1,\dots,i_s}=\frac{D_{i_1,\dots,i_s}}{D},\qquad 1\le i_1<\dots<i_s\le m$

Comparison of the methods

	local	**Morris**	**MC LHS**	**HDMR**
input variance	✓	✓	✓	✓
input *pdf*	✗	✗	✓	✓
output *pdf*	✗	✗	✓	✗
output variance	✓(linear)	✗	✓	✓(biased)
CPU requirement?	✓ **1**	**2110**	**3000**	**16280**
Individual contributions	✓ (linear)	✓(only qualitative)	✗	✓
global?	✗	✓	✓	✓
info about the non-linearities	✗	✓(only qualitative)	✗	✓

Uncertainty analysis: What is it good for?

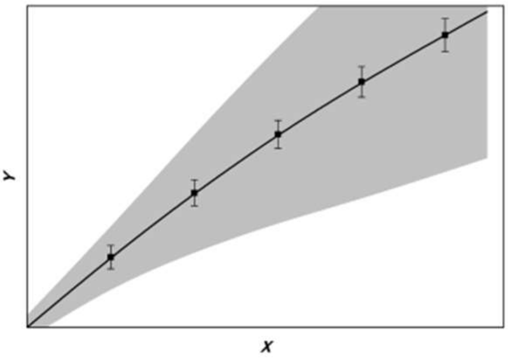
Is the structure of the model OK?



if the experimental data are correct and
if the uncertainty regions of the parameters are well known
BUT the uncertainty regions of measured and simulated results
do not overlap ⇒ the structure of the model is bad (wrong equations!)

What is it good for? 2

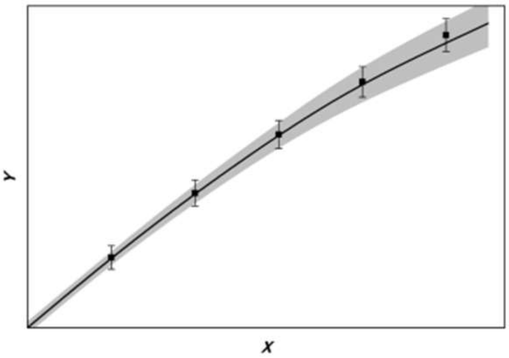
Is the model well established?



if the uncertainty of the simulated results is much wider than
the uncertainty of the data
⇒ any simulation result can be obtained with the parameters
⇒ the model is not useful

What is it good for? 3

Are the model parameters well known?



the uncertainty ranges of the data overlap with the uncertainty of the simulation results; the two uncertainty ranges are similar

⇒ the model is OK,
but the uncertainty of the simulation results can be decreased,
if the critical parameters (to be identified by uncertainty analysis)
are determined with smaller uncertainty

Summary of uncertainty analysis methods

Local uncertainty analysis

one parameter is changed at a time;
based on partial derivatives
can be calculated quickly

Screening methods

several parameters are changed in wide parameter ranges
intermediate computer time requirement
Morris method

Global uncertainty analysis

all parameters are changed simulataneously
according to their joint *pdf*
requires much computer time
e.g. Monte Carlo method (with Latin hypercube sampling)

Example: the uncertainty of methane flame simulation results

The investigated methane flames:

- one dimensional, adiabatic, freely propagating, laminar, premixed stationary flame investigated at equivalence ratios $\varphi = 0.70$ (lean), 1.00 (stoichiometric), and 1.20 (rich)
- cold boundary conditions $p = 1.0$ atm and $T = 298.15$ K

Monitored outputs:

- laminar flame velocity
- maximum temperature
- maximum species concentration of H, O, OH, CH, CH_2

Uncertainty analysis of a laminar methane flame

Leeds Methane Oxidation Mechanism:
37 species and 175 reversible reactions
stationary, laminar 1D simulations

37 species: the recommended values of the enthalpies of formation and their variance was calculated from thermodynamic databases

175 reactions: uncertainty parameteres *f* were collected from Baulch *et al.*

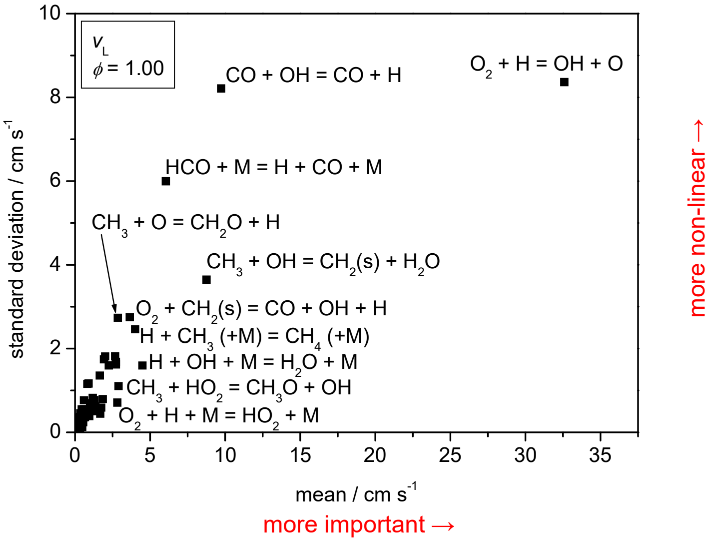
The investigated simulation results:
maximal flame temperature, laminar flame velocity,
maximal concentrations of radicals H, O, OH, CH, CH_2

Uncertainty analysis methods:
local uncertainty analysis, Morris' method,
Monte Carlo with Latin Hypercube sampling, sensititivty indices

J. Zádor, I. Gy. Zsély, T. Turányi, M. Ratto, S. Tarantola, A. Saltelli: Local and global uncertainty analyses of a methane flame model, *J. Phys. Chem. A*, **109**, 9795-9807 (2005)

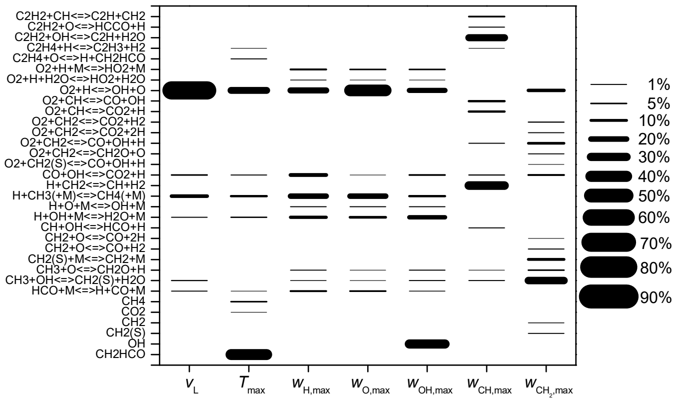
Morris’ method results (φ=1)

contribution of parameter uncertainties to the uncertainty of the flame velocity



Local uncertainty analysis results

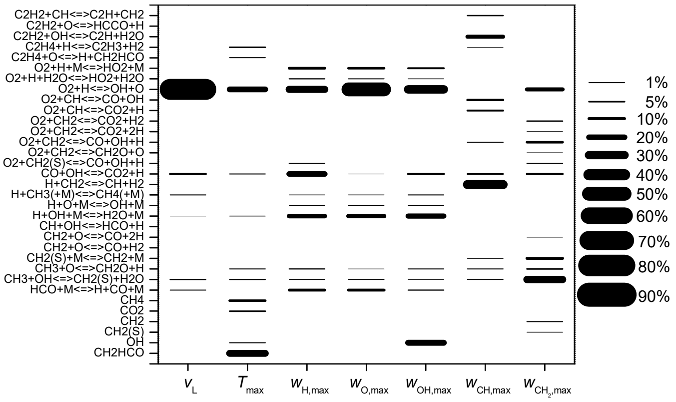
% contribution of parameter uncertainties to the uncertainty of the simulated results



$\varphi = 1.0$

Uncertainty indices

% contribution of parameter uncertainties to the uncertainty of the simulated results



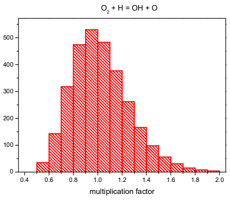
$\varphi = 1.0$

Assumed probability density functions of kinetic and thermodynamic parameters

The Monte Carlo and the sensitivity index methods
require an assumption on the
probability density functions (*pdf*s) of parameters

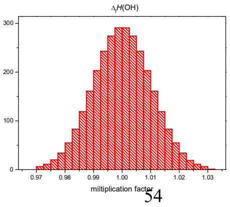
Rate coefficients:

- log-normal distribution
- σ_j was calculated from the f_j uncertainty factor
- the log-normal distribution is clipped at $\pm 3\sigma (\ln k_j)$

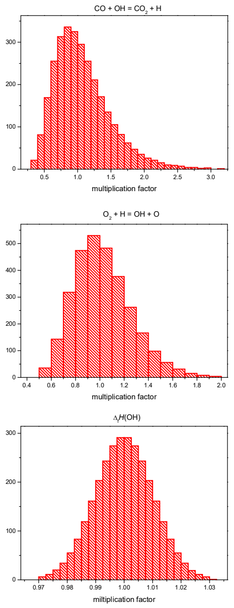


Enthalpies of formation:

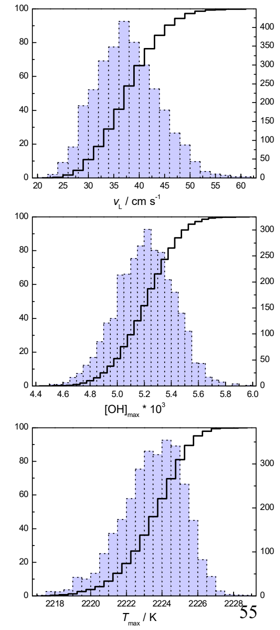
- normal distribution
- σ is assessed on the basis of thermodynamic tables
- the normal distribution is clipped at $\pm 3\sigma$



pdf of parameters



pdf of simulation results

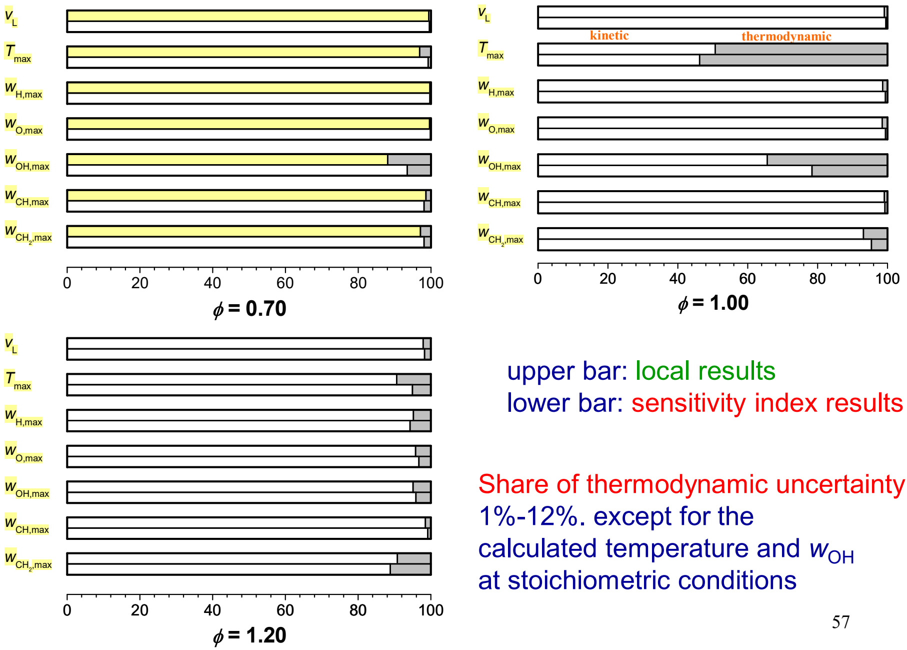


3,000 Monte Carlo simulations

Comparison of the results of local and global (Monte Carlo) uncertainty analyses for a stoichiometric, stationary, flat methane-air flame

	result	calculated variances from local	 Monte Carlo
		uncertainty analyses	
flame velocity	38.1 cm/s	4.6 cm/s	6.2 cm/s
max. T	2224.2 K	2.8 K	1.7 K
max. w_H	2.14×10^{-4}	14.7%	12.6%
max. w_O	1.74×10^{-3}	13.3%	10.4%
max. w_{OH}	5.27×10^{-3}	3.6%	4.0%
max. w_{CH}	8.07×10^{-7}	46.3%	49.2%
max. w_{CH2}	2.54×10^{-5}	23.8%	24.0%

Kinetic *vs.* thermodynamic contributions



upper bar: local results
lower bar: sensitivity index results

Share of thermodynamic uncertainty: 1%-12%. except for the calculated temperature and w_{OH} at stoichiometric conditions

Methane flame uncertainty analysis: general conclusions

Good agreement between the calculated total variances by the local uncertainty analysis and the Monte Carlo method. (surprise)

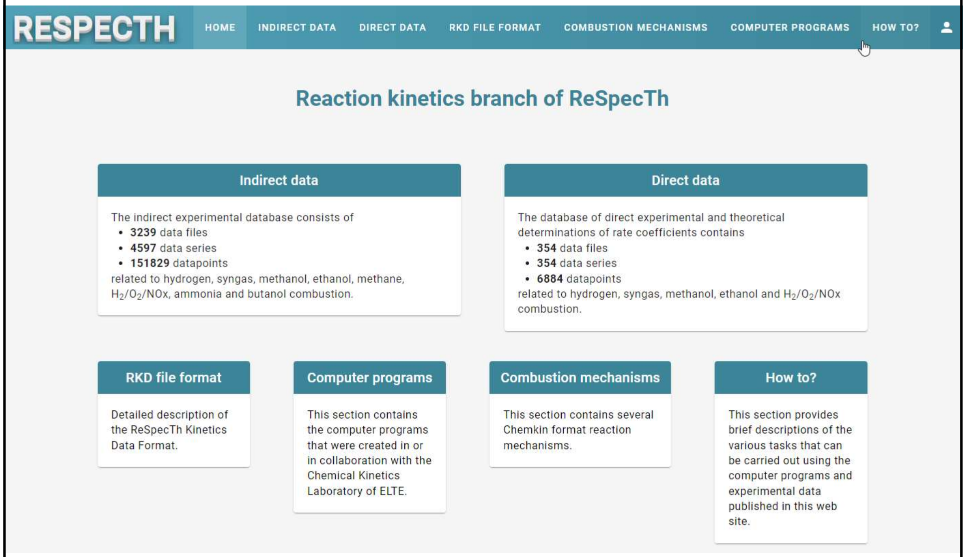
Good agreement between the importance of parameters assessed by the local uncertainty analysis and the sensitivity indices. (surprise)

Better simulation results can be achieved, if the rate coefficients of a few reactions and the enthalpies of formation of a few species are known better (= with smaller variance)
These represent a small fraction of the total number of species/reactions.

Significant rate coefficients:
$O_2 + H = OH + O$
$O_2 + H + M = HO_2 + M$
$CO + OH = CO_2 + H$
$H + CH_3 + M = CH_4 + M$
$CH_3 + OH = CH_2(S) + H_2O$
$C_2H_2 + OH = C_2H + H_2O$
$C_2H_2 + CH = C_2H + CH_2$
$H + CH_2 = CH + H_2$

Significant enthalpies of formation:
OH
$CH_2(S)$
CH_2
CH_2OH
CH_2CHO

Reaction kinetics branch of the ReSpecTh web site https://respecth.hu



Reaction kinetics branch of ReSpecTh

Indirect data

The indirect experimental database consists of
- **3239** data files
- **4597** data series
- **151829** datapoints

related to hydrogen, syngas, methanol, ethanol, methane, $H_2/O_2/NOx$, ammonia and butanol combustion.

Direct data

The database of direct experimental and theoretical determinations of rate coefficients contains
- **354** data files
- **354** data series
- **6884** datapoints

related to hydrogen, syngas, methanol, ethanol and $H_2/O_2/NOx$ combustion.

RKD file format

Detailed description of the ReSpecTh Kinetics Data Format.

Computer programs

This section contains the computer programs that were created in or in collaboration with the Chemical Kinetics Laboratory of ELTE.

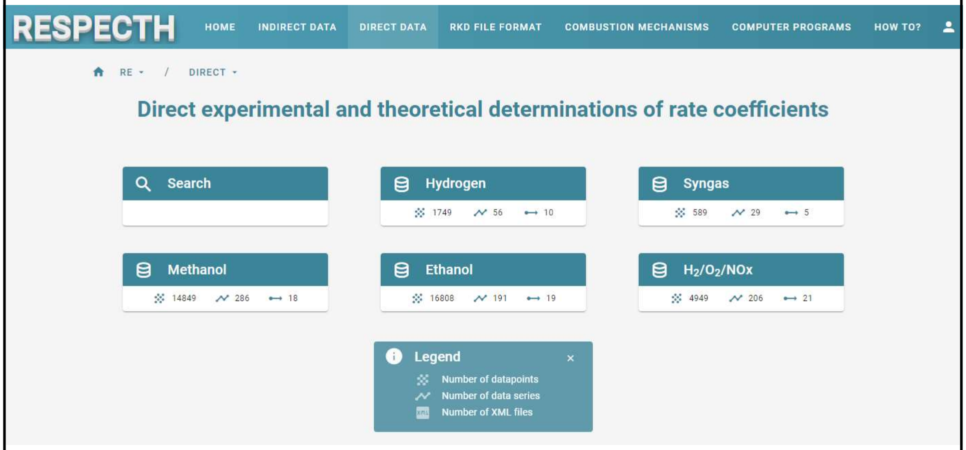
Combustion mechanisms

This section contains several Chemkin format reaction mechanisms.

How to?

This section provides brief descriptions of the various tasks that can be carried out using the computer programs and experimental data published in this web site.

Experimental and theoretical rate determinations

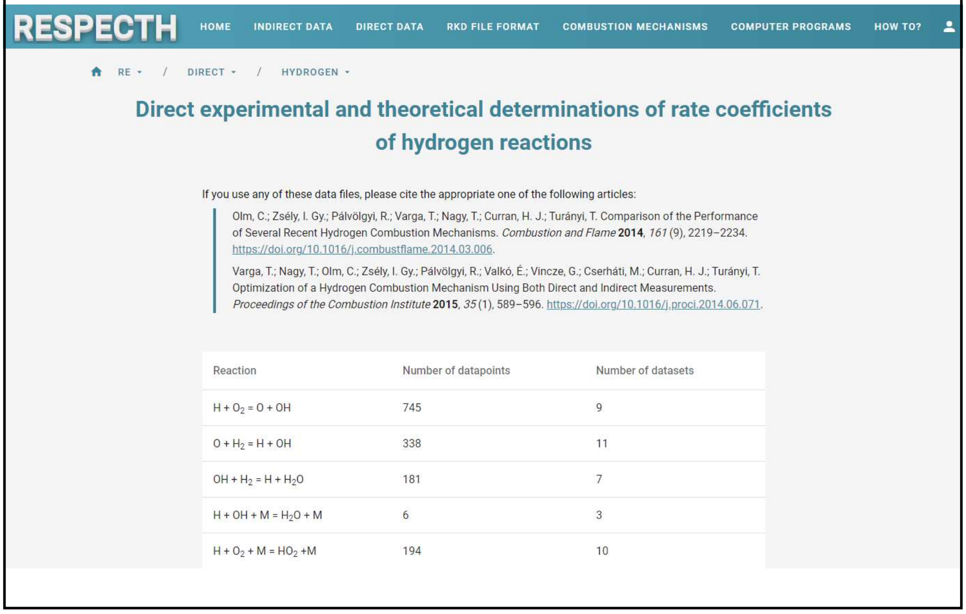


Direct experimental and theoretical determinations of rate coefficients

	Number of datapoints	Number of data series	Number of XML files
Hydrogen	1749	56	10
Syngas	589	29	5
Methanol	14849	286	18
Ethanol	16808	191	19
$H_2/O_2/NOx$	4949	206	21

Legend
- Number of datapoints
- Number of data series
- Number of XML files

Experimental and theoretical rate determinations – Hydrogen



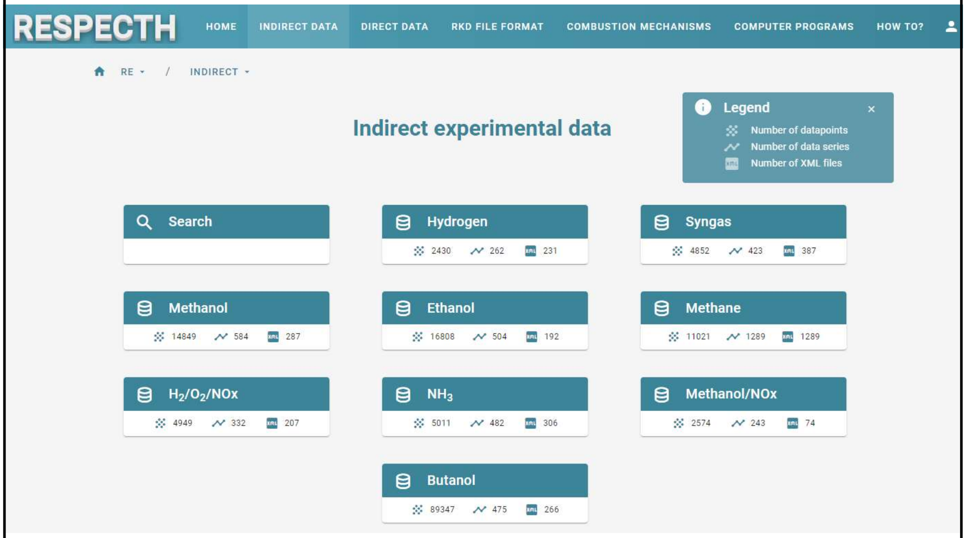
Direct experimental and theoretical determinations of rate coefficients of hydrogen reactions

If you use any of these data files, please cite the appropriate one of the following articles:

> Olm, C.; Zsély, I. Gy.; Pálvölgyi, R.; Varga, T.; Nagy, T.; Curran, H. J.; Turányi, T. Comparison of the Performance of Several Recent Hydrogen Combustion Mechanisms. *Combustion and Flame* **2014**, *161* (9), 2219–2234. https://doi.org/10.1016/j.combustflame.2014.03.006.
>
> Varga, T.; Nagy, T.; Olm, C.; Zsély, I. Gy.; Pálvölgyi, R.; Valkó, É.; Vincze, G.; Cserháti, M.; Curran, H. J.; Turányi, T. Optimization of a Hydrogen Combustion Mechanism Using Both Direct and Indirect Measurements. *Proceedings of the Combustion Institute* **2015**, *35* (1), 589–596. https://doi.org/10.1016/j.proci.2014.06.071.

Reaction	Number of datapoints	Number of datasets
$H + O_2 = O + OH$	745	9
$O + H_2 = H + OH$	338	11
$OH + H_2 = H + H_2O$	181	7
$H + OH + M = H_2O + M$	6	3
$H + O_2 + M = HO_2 + M$	194	10

Indirect combustion experimental data



Indirect experimental data

Hydrogen 2430 262 231

Syngas 4852 423 387

Methanol 14849 584 287

Ethanol 16808 504 192

Methane 11021 1289 1289

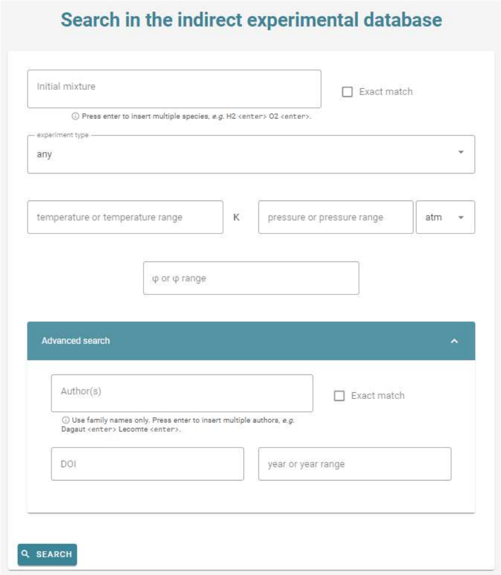
$H_2/O_2/NOx$ 4949 332 207

NH_3 5011 482 306

Methanol/NOx 2574 243 74

Butanol 89347 475 266

Indirect combustion experimental data
Search engine



Search in the indirect experimental database

Initial mixture ☐ Exact match

ⓘ Press enter to insert multiple species, e.g. H2 <enter> O2 <enter>.

experiment type: any

temperature or temperature range K

pressure or pressure range atm

φ or φ range

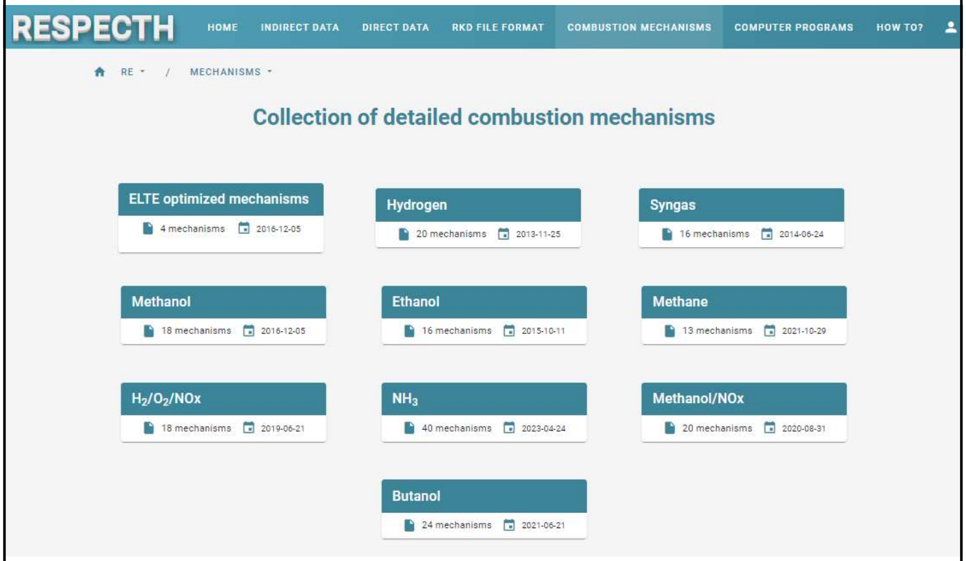
Author(s) ☐ Exact match

ⓘ Use family names only. Press enter to insert multiple authors, e.g. Dagaut <enter> Lecomte <enter>.

DOI

year or year range

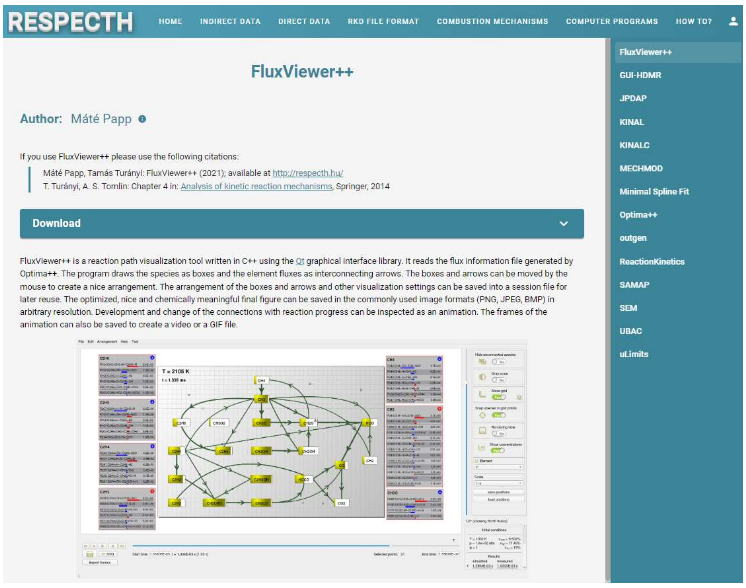
Combustion mechanisms



Collection of detailed combustion mechanisms

ELTE optimized mechanisms	4 mechanisms	2016-12-05
Hydrogen	20 mechanisms	2013-11-25
Syngas	16 mechanisms	2014-06-24
Methanol	18 mechanisms	2016-12-05
Ethanol	16 mechanisms	2015-10-11
Methane	13 mechanisms	2021-10-29
$H_2/O_2/NOx$	18 mechanisms	2019-06-21
NH_3	40 mechanisms	2023-04-24
Methanol/NOx	20 mechanisms	2020-08-31
Butanol	24 mechanisms	2021-06-21

Computer programs



FluxViewer++

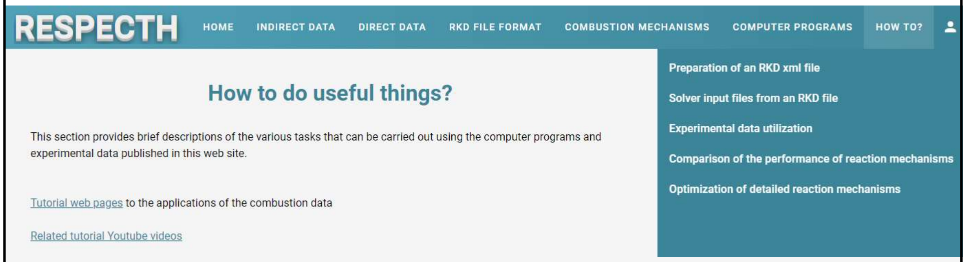
Author: Máté Papp

If you use FluxViewer++ please use the following citations:

> Máté Papp, Tamás Turányi: FluxViewer++ (2021); available at http://respecth.hu/
> T. Turányi, A. S. Tomlin: Chapter 4 in: Analysis of kinetic reaction mechanisms, Springer, 2014

FluxViewer++ is a reaction path visualization tool written in C++ using the Qt graphical interface library. It reads the flux information file generated by Optima++. The program draws the species as boxes and the element fluxes as interconnecting arrows. The boxes and arrows can be moved by the mouse to create a nice arrangement. The arrangement of the boxes and arrows and other visualization settings can be saved into a session file for later reuse. The optimized, nice and chemically meaningful final figure can be saved in the commonly used image formats (PNG, JPEG, BMP) in arbitrary resolution. Development and change of the connections with reaction progress can be inspected as an animation. The frames of the animation can also be saved to create a video or a GIF file.

How to ...



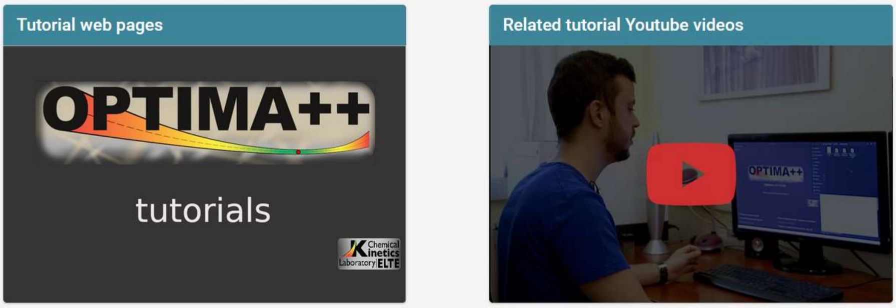
How to do useful things?

This section provides brief descriptions of the various tasks that can be carried out using the computer programs and experimental data published in this web site.

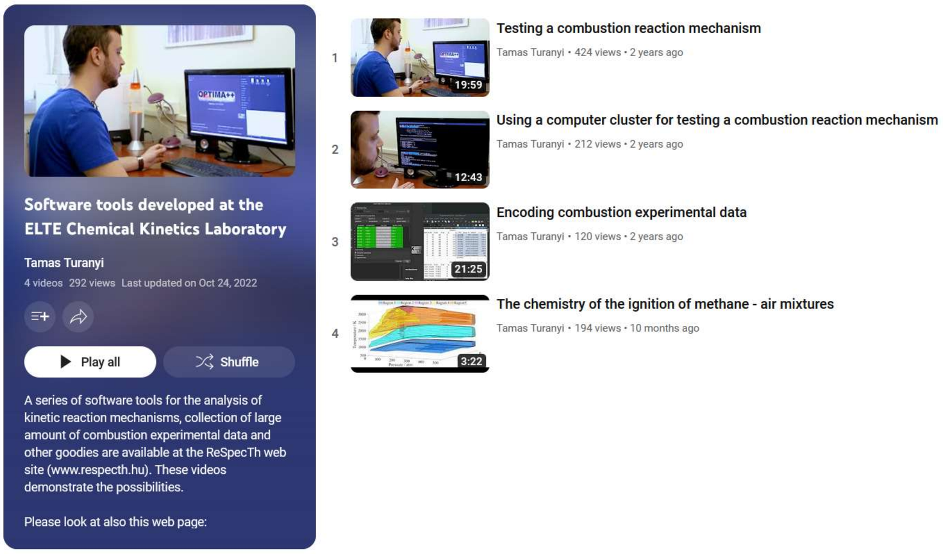
Tutorial web pages to the applications of the combustion data

Related tutorial Youtube videos

This section provides brief descriptions of the various tasks that can be carried out using the computer programs and experimental data published in this web site.



Tutorial videos



Software tools developed at the ELTE Chemical Kinetics Laboratory

Tamas Turanyi

4 videos 292 views Last updated on Oct 24, 2022

A series of software tools for the analysis of kinetic reaction mechanisms, collection of large amount of combustion experimental data and other goodies are available at the ReSpecTh web site (www.respecth.hu). These videos demonstrate the possibilities.

Please look at also this web page:

1 Testing a combustion reaction mechanism
Tamas Turanyi • 424 views • 2 years ago
19:59

2 Using a computer cluster for testing a combustion reaction mechanism
Tamas Turanyi • 212 views • 2 years ago
12:43

3 Encoding combustion experimental data
Tamas Turanyi • 120 views • 2 years ago
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4 The chemistry of the ignition of methane - air mixtures
Tamas Turanyi • 194 views • 10 months ago
3:22

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for your attention!