

Presto-Kinetics 11

An overview of features and capabilities

How to contact us

Contact us for more information!

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What is Presto-Kinetics?

▶ Open solver for...

- ▶ Basic chemical kinetics
- ▶ Bio kinetics and systems biology
- ▶ Reactor models (batch, semi-batch, continuous, plug-flow, cascades)

▶ Contains modules for...

- ▶ kinetics
- ▶ phase changes
- ▶ mass transfers
- ▶ particle growth
- ▶ reactor flows
- ▶ spatial profiles

▶ Includes...

- ▶ A solver for partial differential equations
- ▶ A framework for multiple-phase systems
- ▶ Sophisticated parameter estimation based on unique algorithm



The Presto-Kinetics 11 user interface

The screenshot displays the Presto-Kinetics 11 software interface, which is used for simulating chemical reactions. The main window is titled "Presto-Kinetics 11 by CiT" and features a menu bar (File, Project, Simulation, Tools, Navigation) and a toolbar with various simulation controls like "Debug mode", "Start", "Stop", and "Restart".

Key components of the interface include:

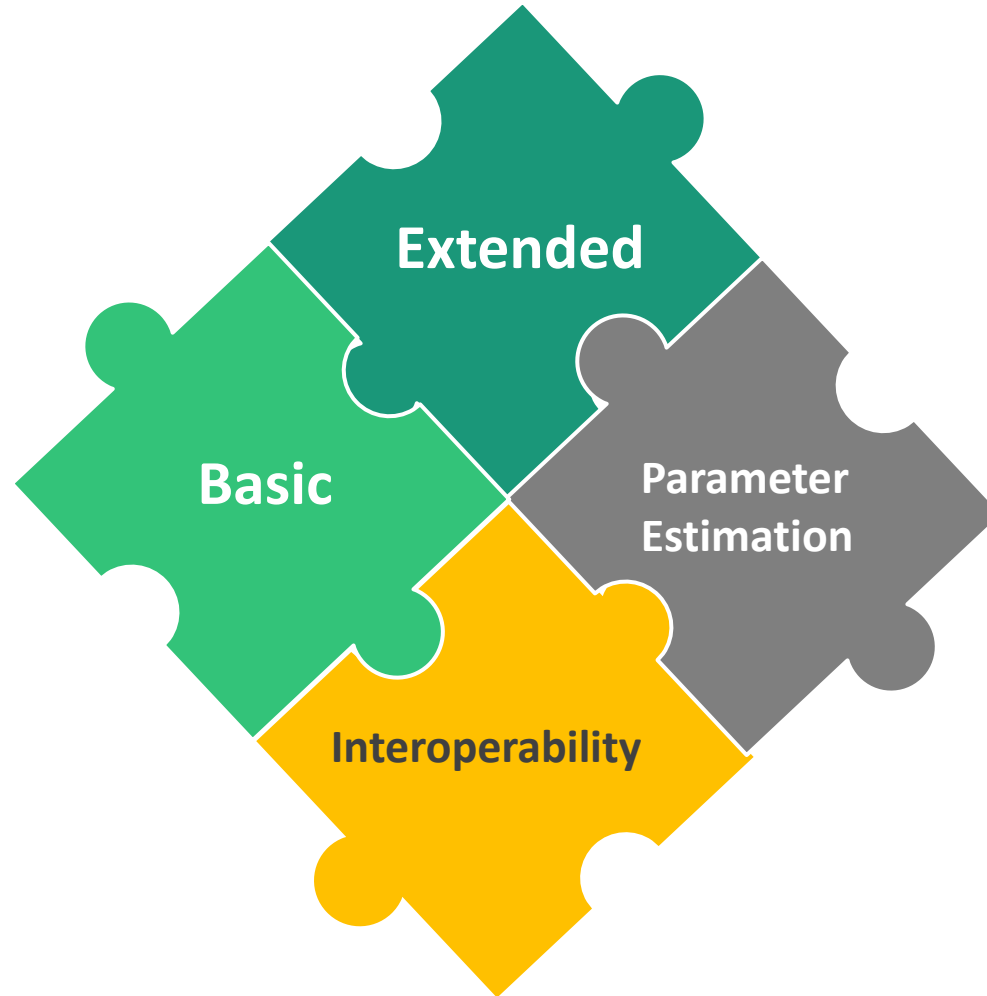
- Graphs (Model: Oregonator.xml):** Shows concentration profiles for various species over time. The x-axis represents time (T [s]) and the y-axis represents concentration (Conc [mol/l]).
- Model/Simulation PE + Optimization + Sensitivity analysis:** A central panel for configuring the simulation, including a table of reactions and their parameters.
- Reaction step configuration:** A detailed view of a specific reaction step, showing its name, pattern, result, and stoichiometric coefficients.
- Reactor input table:** A table listing substances, their masses, moles, and concentrations.
- Reaction step configuration table:** A table defining the reaction step, including species names, stoichiometric coefficients, and reaction orders.

The reaction step configuration table is as follows:

No.	n _i	A _i	order _i	k _{for} (script)	n _j	B _j	order _j
1	1	Br			2	HBr	
2	1	HBrO2		k1	1	HBr	
3	0				0		
4	1				1		
5	1			k _{back} (script)	1		

The reaction step configuration also includes a "Pattern" field with the chemical equation: $n1A1 + \dots + n5A5 \leftrightarrow m1B1 + \dots + m5B5$ and a "Result" field with the chemical equation: $Br + HBrO2 \leftrightarrow 2HBr$. The stoichiometric coefficients are listed as k1, k2, k3, k4, and k5.

Presto-Kinetics' Features: An overview



Presto-Kinetics' Features: Basic

- ▶ Comprehensive list of **modules** that can be combined with **any type** of kinetics
- ▶ Sophisticated “all-in-one” model and **project administration**, including handling of alternative models and parameters, reaction groups, model comparison and much more
- ▶ **Dynamic outputs** that reflect all structures of a model by a configurable chart administration
- ▶ Comprehensive **recipe** modules that control the full setup of a simulation and can easily be organized, selected, edited and copied
- ▶ Open **script** interpreter with powerful commands for user-defined outputs, reaction rates and equations



Presto-Kinetics' Features: Extended

- ▶ Model **sensitivity** analysis: different methods
- ▶ **Recipe variation** tool to compare **process** strategies
- ▶ PDE-solver for **spatial profiles**, e.g. in stationary tubular reactors or concentrations in films or particles



Presto-Kinetics' Features: Parameter Estimation

- ▶ Fitting of any number and any type of **parameter**
- ▶ Administration of any number and type of **experiments**
- ▶ Comparison of any model and data type
- ▶ **Global** search algorithms
- ▶ **Proprietary** local search **algorithm** with correlation analysis used for 20 years
- ▶ Efficient **uncertainty** and sampling algorithms

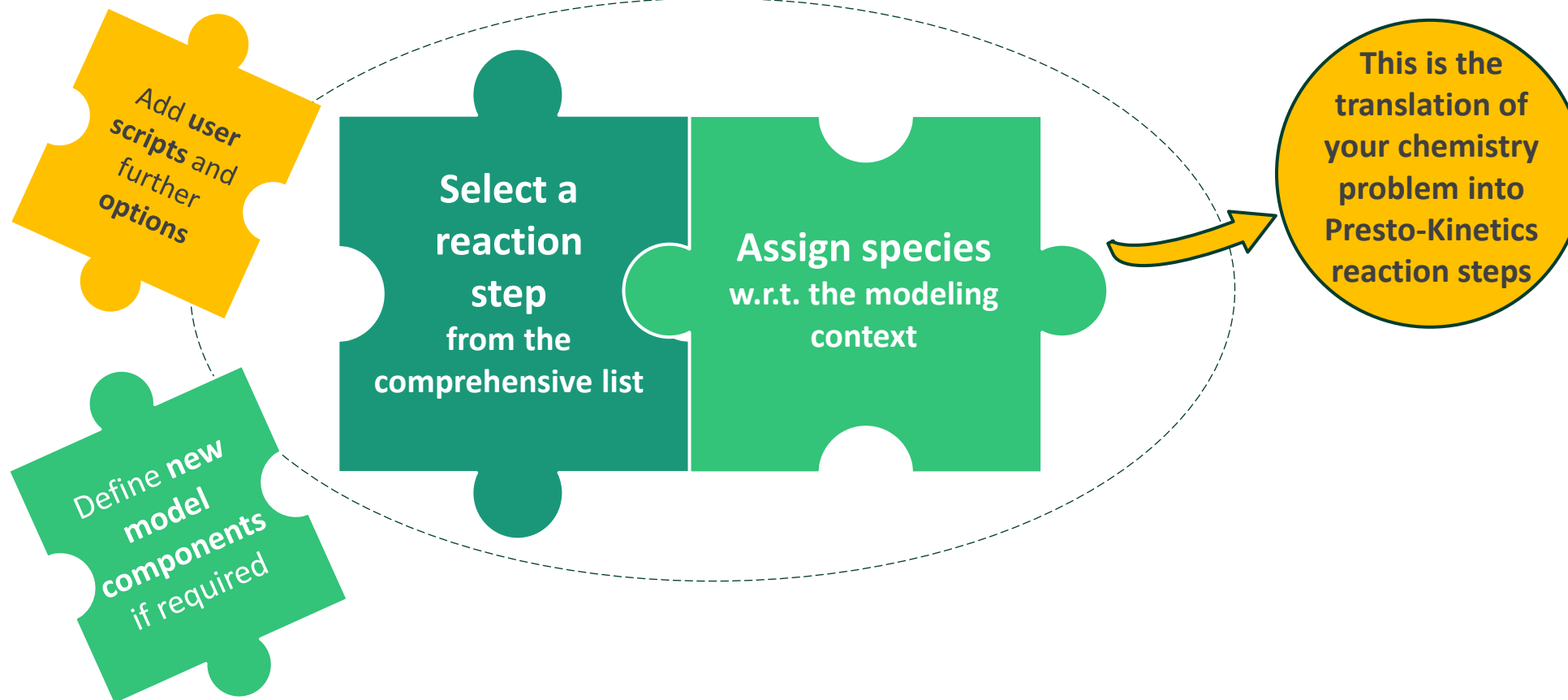


Presto-Kinetics' Features: Interoperability

- ▶ Output of all results and data to **Excel** and text files
- ▶ **Cape-Open** interface to access thermodynamic tools, in particular **Multiflash** by KBC
- ▶ **OLE/COM** interface to control Presto-Kinetics from third-party software, e.g. Excel, Matlab, Python, C++
- ▶ Script **export** of core model equations (moment-based) to Matlab or C
- ▶ User **database** for parameters and substance data to organize model inputs

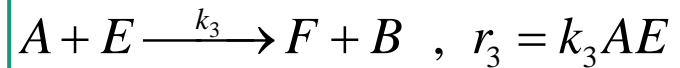
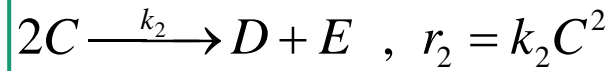
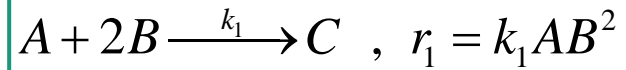


Modular kinetics: Add one reaction step



Modular system for kinetics

Typical scheme



Differential equations (ODEs)

$$A' = -r_1 - r_3 = -k_1 AB^2 - k_3 AE$$

$$B' = -2r_1 + r_3 = -2k_1 AB^2 + k_3 AE$$

$$C' = r_1 - 2r_2 = k_1 AB^2 - 2k_2 C^2$$

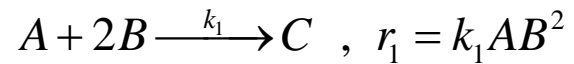
$$D' = r_2 = k_2 C^2$$

$$E' = r_2 - r_3 = k_2 C^2 - k_3 AE$$

$$F' = r_3 = k_3 AE$$

Presto-Kinetics approach

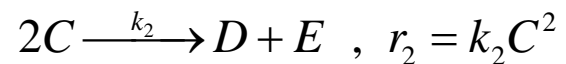
- ▶ Single reactions **derive their “own” ODEs** internally
- ▶ Once a kinetic step pattern is implemented and validated, it can be used **again and again**
- ▶ Reaction rates can be **arbitrarily complex**
- ▶ **Equilibrium reactions** are supported
- ▶ All terms are **superposed**, even kinetic steps and abstract ODEs
- ▶ All further terms are **added automatically**
- ▶ **Internal treatment** of species is based on mol/volume



$$A' = -k_1 r AB^2$$

$$B' = -2k_1 AB^2$$

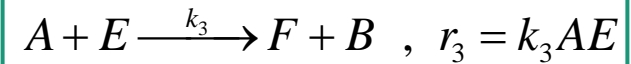
$$C' = k_1 AB^2$$



$$C' = -2k_2 C^2$$

$$D' = k_2 C^2$$

$$E' = k_2 C^2$$



$$A' = -k_3 AE$$

$$E' = -k_3 AE$$

$$B' = k_3 AE$$

$$F' = k_3 AE$$

Modular kinetics

- ▶ Select reaction step pattern from list using, e.g. “General kinetic”

No.	Name	Pattern	Flow	Moment's cl...	Copolymeriz...	Profile
1	CollectedFlow	R1 ==> R2 , k1[Script] = split	X			
2	CollectedFlow(low)	R1 ==> R2 , k1[Script] = split	X			
3	CollectedFlow_direct	R1 ==> R2 , k1[Script] = flowrate	X			
4	Elementalreaction	A (+ B) -> C (+ D), k1[File]				
5	Flow(low)	A ==> B , k1[Script] = split	X			
6	FluidExitStream	A ==> (out) , k1[Script] = mass/time				
7	Kinetic	n1A1 + ... + n5A5 <-> m1B1 + ... + m5B5				
8	Masstransfer	A ==> (B) , k1[Script] = mass/time				
9	ODE-System	y' = f[Script](y)				
10	ODE-System-Reactor	y' = f[Script](y)				
11	PDE-Agglomeration	u(x) + u(y) -> v(x+y) , k1[Script](x,y)		yes		X
12	PDE-AgglomerationL	u(x) + u(y) -> v(x^3+y^3)^1/3 , k1[Script2]*Scri...		yes		X
13	PDE-Breakage	u(x) -> v(y) + w(x-y) , k1[Script](x,y)		no		X
14	PDE-Connect	u(xMin,t) = k1[Script]*v(xMax,t)		yes		X
15	PDE-Convection	d/dt u(x,t) = -k1 * Script() * Script(x) * d/dx u(x,t)		yes		X
16	PDE-Convection2	d/dt u(x,t) = -k1 * Script2(x) * d/dx (Script(x)*u(x,t))		yes		X
17	PDE-Diffusion	d/dt u(x,t) = k1[Script] * d^2/dx^2 u(x,t)		yes		X
18	PDE-Diffusion2	d/dt u(x,t) = k1[Script] * Script2(x) * d^2/dx^2 u...		yes		X
19	PDE-Dirichlet-left	u(0,t) = k1[Script](c)		yes		X
20	PDE-Dirichlet-right	u(xMax,t) = k1[Script]		yes		X
21	PDF-FeedProfile	==u[Script1]*k1==> u(x) k1[Script2] = con		yes		X

- ▶ Assign species w.r.t modeling context

Reaction step of Oregonator.xml

Name: General kinetic step for elemental species

Pattern: $n1A1 + \dots + n5A5 \leftrightarrow m1B1 + \dots + m5B5$

Result: $Br + HBrO2 \leftrightarrow 2 * HBr, k2, 0$

No.	n_i	A_i	order_i	m_i	B_i	order_i
1		Br		2	HBr	
2						
3						
4						
5						

Script [+Enthalpy]:

Reaction law rp:

Equilibrium

Comment:

Active

Backw Forward

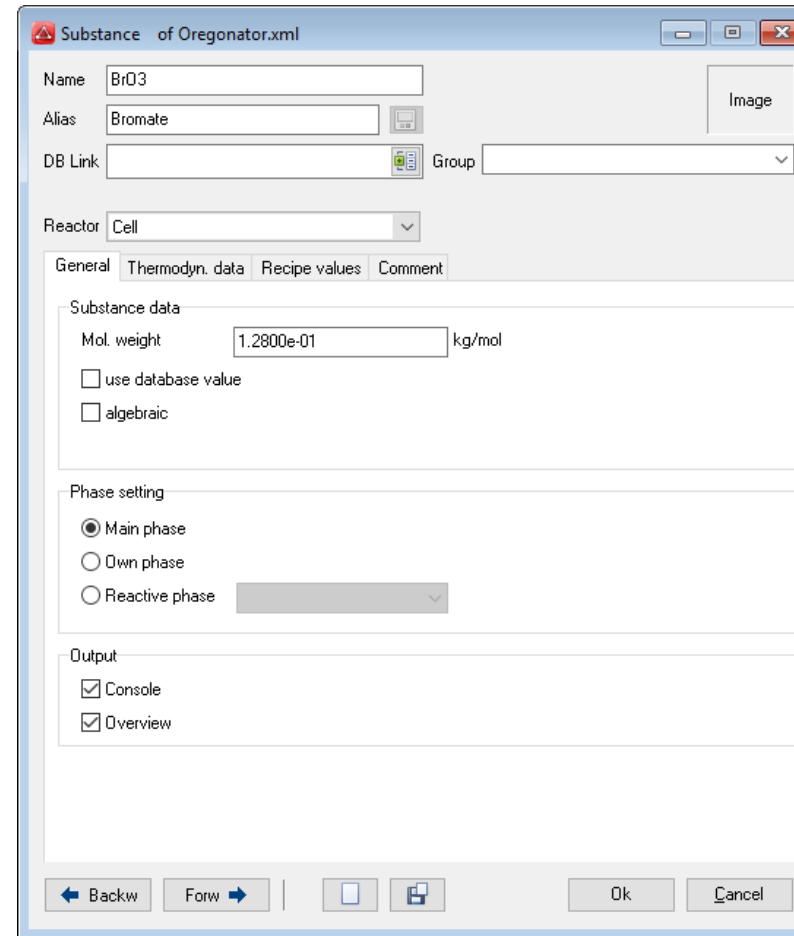
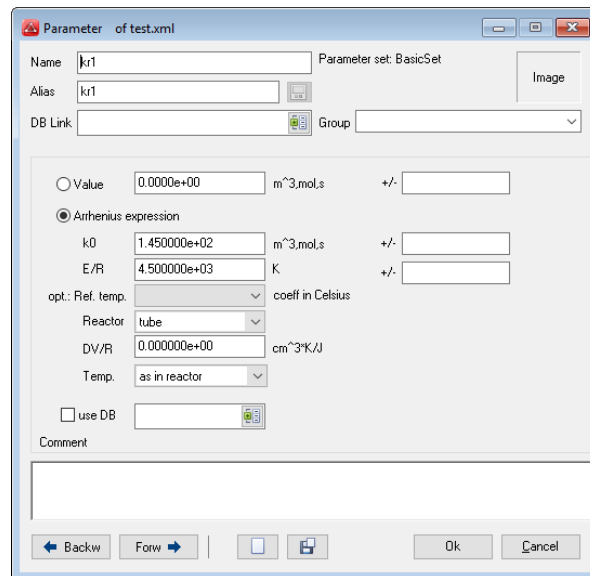
Select a property

New:

No.	Group	Name	Alias/DB link	Reactor
1		Br	Bromine	Cell
2		BrO3	Bromate	Cell
3		HBrO2	Bromous_acid	Cell
4		HBr	Hypobromous_...	Cell
5		Ce	Cerium	Cell
6		S	Solvent	Cell

Model administration – components

- ▶ Various properties and settings
- ▶ Comfortable editing
- ▶ Access to user-database
- ▶ Extension by user-scripts possible



Dynamic output of results

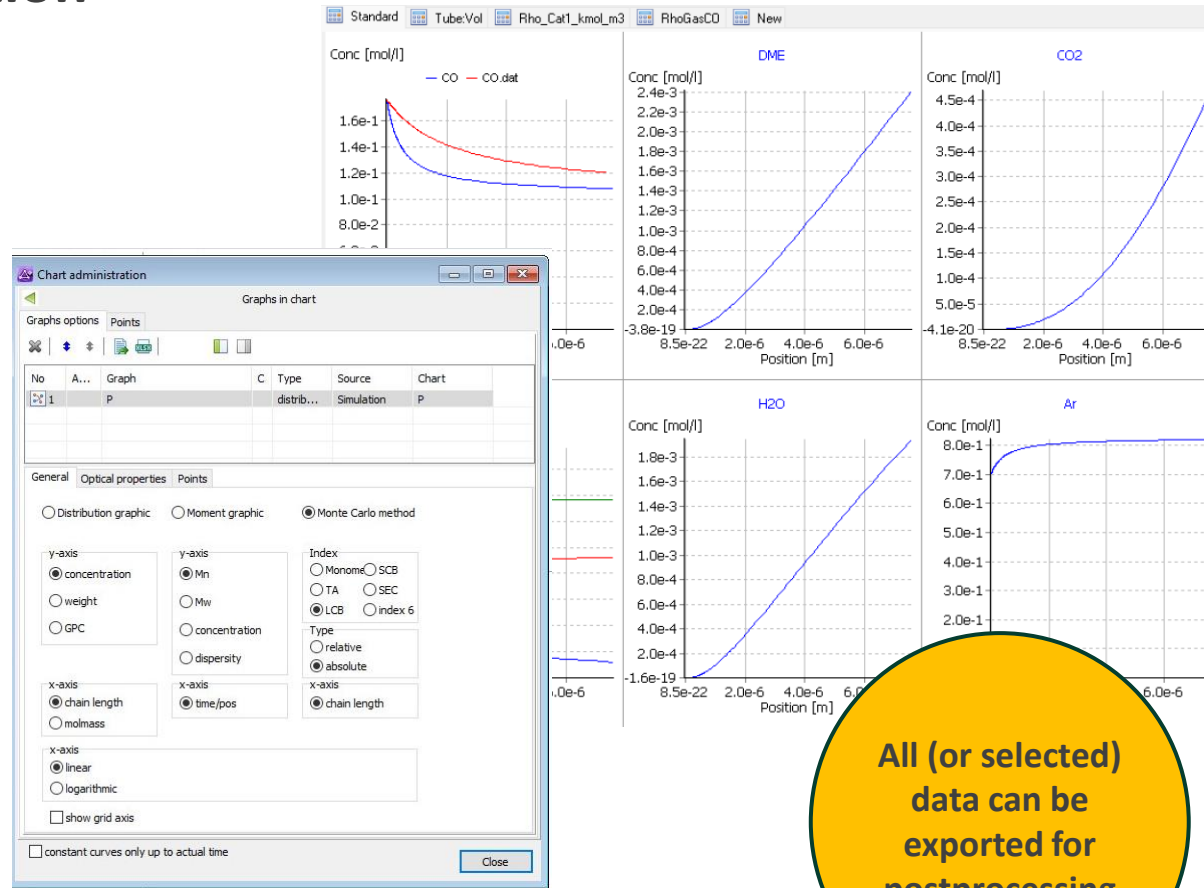
Create your own chart selection

Choose from a comprehensive list of graphical representations

Combine different graphics in one chart

Compare to reference results from other simulations

All changes of the graphical representation can be done live (i.e. while simulations are running)



All (or selected) data can be exported for postprocessing

Recipes: Overview

- ▶ Recipes provide reactor operations and model scenarios
- ▶ All inputs of all species are entered in recipes
- ▶ Each project contains a list of recipes, only one is set to be the active recipe
- ▶ Various feed strategies are possible – from a simple feed to control of properties

Basic definition Additional info Process Control

Tube

Operation mode: tube reactor
Temperature [°C]: constant 240
Pressure [bar]: constant 50
Exit stream [l/s]: (none) 0.00000e+00

Reactor input

Composition of tank: Reactor input

Substances	Part (mass)	Masses [g]	Part (mole)	Moles	Concentration [mol/l]	Mole mass [g/mole]	Density [g/l]
CO	6.081e-01	1.441e-03	1.500e-01	5.147e-06	1.758e-01	280.01000	328.14445
H2	4.377e-03	1.037e-05	1.500e-01	5.147e-06	1.758e-01	2.01580	2.36232
CH3OH	0	0	0	0	0	32.04200	37.55010
DME	0	0	0	0	0	46.06900	53.98838
H2O	0	0	0	0	0	18.01500	21.11183
CO2	0	0	0	0	0	44.01000	51.57543
N2	4.056e-02	9.612e-05	1.000e-01	3.431e-06	1.172e-01	28.01300	32.82851
Ar	3.470e-01	8.224e-04	6.000e-01	2.059e-05	7.031e-01	39.94800	46.81517
Cat1	0	0	0	0	0	101.96000	1000.00000
Cat2	0	0	0	0	0	81.38900	1000.00000

Recipes: Overview

Temperature and pressure control possible

Input can be entered for species, particles or profiles

Open number of feed tanks with individual composition

Direct conversion of various input types

Substances	Part (mass)	Masses [kg]	Part (mole)	Moles	Concentration [mol/l]	Mole mass [kg/mole]	Absolute moles
H2O	4.276e-01	9.00000e-01	7.933e-01	500.00000	26.24658	1.800e-02	1.000e+00
I	2.375e-03	5.000e-02	3.967e-04	2.500e-01	1.312e-02	2.000e-01	1.000e+00
Is	0	0	0	0	0	1.000e-01	1.000e+00
Ip	0	0	0	0	0	1.000e-01	1.000e+00
IpFrag	0	0	0	0	0	1.000e-01	1.000e+00
M1	4.751e-01	10.00000	1.587e-01	100.00000	5.24932	1.000e-01	1.000e+00
M2	4.751e-06	1.000e-04	3.173e-06	2.000e-03	1.050e-04	5.000e-02	1.000e+00
M1p	0	0	0	0	0	1.000e-01	1.000e+00
M2p	0	0	0	0	0	5.000e-02	1.000e+00
M1drop	0	0	0	0	0	1.000e-01	1.000e+00
M2drop	4.751e-02	1.000e+00	3.173e-02	20.00000	9.501e-01	5.000e-02	1.000e+00
Seed	4.751e-02	1.000e+00	1.587e-02	10.00000	10.00000	1.000e-01	1.000e+00
C1	0	0	0	0	0	0	1.000e+00
C2	0	0	0	0	0	0	1.000e+00
Rw1	0	0	0	0	0	0	1.000e+00
Sum		21.05010		630.25200			1.000e+00
Volume [l]					21.05010		

Parameter estimation in Presto-Kinetics

Presto-Kinetics has the most sophisticated PE for kinetics

- ▶ **Full project administration** with many options and algorithms
- ▶ Adjust **any number** of parameters
- ▶ Use **any number** and **type** of measurements, such as
 - ▶ Concentrations
 - ▶ Other time-dependent data
- ▶ **Methods** include
 - ▶ Gauss-Newton algorithm with proprietary extensions
 - ▶ Simulated Annealing
 - ▶ Bayesian analysis

Parameter estimation steps



Parameter estimation is also called parameter...

- identification
- fitting
- tuning
- calibration
- optimization



Experiments in Presto-Kinetics

- ▶ One data set per experiment (MDF)
- ▶ Free assignment of data columns to (scripted) outputs (modeled sensors)
- ▶ MDFs are combined to PE configurations

Name:

Additional control by key words

Measured data

	1	2	3	4	5	6
scale		0	0	0	0	0
weight		5	-1	-1	-1	-1
penalty		0	0	0	0	0
pol		1	1	1	1	1
	times	total_Mw	Ini_R_frac	m1wpct	m2wpct	TMBSppm
1	3600	-1	-1	18.41851149	11.33177483	-1
2	7200	-1	-1	15.71295619	9.806010513	-1
3	10800	-1	-1	12.82765108	8.589624022	-1
4	14400	-1	-1	12.20618262	7.549662055	-1
5	18000	-1	-1	11.14499472	6.477149505	-1
6	21600	-1	-1	10.23570388	5.66726228	-1
7	25200	-1	-1	9.359515565	5.361867305	-1
8	28800	-1	-1	7.917038163	4.626164083	-1
9	32400	-1	-1	7.59108151	4.360596023	-1
10	36000	-1	-1	6.841092198	3.671480421	-1
11	39600	15.74812771	0.017256068	6.194027575	3.356177545	153.7808348

Map
experimental
data to
model

Model/Simulation PE + Optimization + Sensitivity analysis

Estimation Optimization

Estimation definitions (former *.par)

No.	Name	# Parameter	# Robust parameter	# Act. data files
1	FitMinimal1_Copy	6	0	6
2	Test3Signals	6	0	3
3	Test3Signals_Ini2	6	0	3
4	Test3Signals5Exp	6	0	6
5	Test3Signals_TMBS	6	0	3
6	Test3Signals_Ini2_TMBS	6	0	3
7	Test3Signals6Exp_TMBS	6	0	6
8	Test3Signals_TMBS_Langevin	6	0	3

Measured data PE Batches Options

Measured data files in PE Synopsis

No.	Name	U..	linked in estimation...	linked to recipe
1	copo_batch_60S_thin_p3		FitMinimal1_Copy....	copo_batch_60S
2	copo_batch_10S_thin_p1		FitMinimal1_Copy....	copo_batch_10S
3	copo_batch_90S_thin_p2		FitMinimal1_Copy....	copo_batch_90S
4	copo_semibatch_50S_MMS_f...		FitMinimal1_Copy....	copo_semibatch_50...
5	copo_semibatch_50S_thin_p1		FitMinimal1_Copy....	copo_semibatch_50S
6	copo_semibatch_50S_S_thin_...		FitMinimal1_Copy....	copo_semibatch_50...

Sensitivity analysis

- ▶ Parameters are considered to be distributions with given **mean value** and **standard deviation**
- ▶ Select parameters and edit standard deviation
- ▶ Monte-Carlo or Sigma-Point analysis describes the range of the model
- ▶ Advantage of Sigma-Point: only $2 \cdot p + 1$ simulations required
- ▶ Alternative for up to 3 parameters: variation on grid

Parameter estimation configuration of DME_Fugacities_Database.xml.xml

Name Sensi1

Coefficients
 Measured data
 Numerical settings
 Reduced direction
 See

No.	Fit?	Name	Initial value in PE	Prefactor(k0)	Energy	No. B
2	<input type="checkbox"/>	2	2.000e+00			
3	<input type="checkbox"/>	k1	1.600e-03			
4	<input checked="" type="checkbox"/>	K1	1.000e+01			
5	<input checked="" type="checkbox"/>	k2	1.000e-04			
6	<input checked="" type="checkbox"/>	K2	1.000e+01			
7	<input checked="" type="checkbox"/>	k3	1.000e-03			
8	<input checked="" type="checkbox"/>	K3	1.000e+01			

show only those which are to be fitted

Fit options

Fit this coefficient with initial value

Variation and sensitivity and Langevin

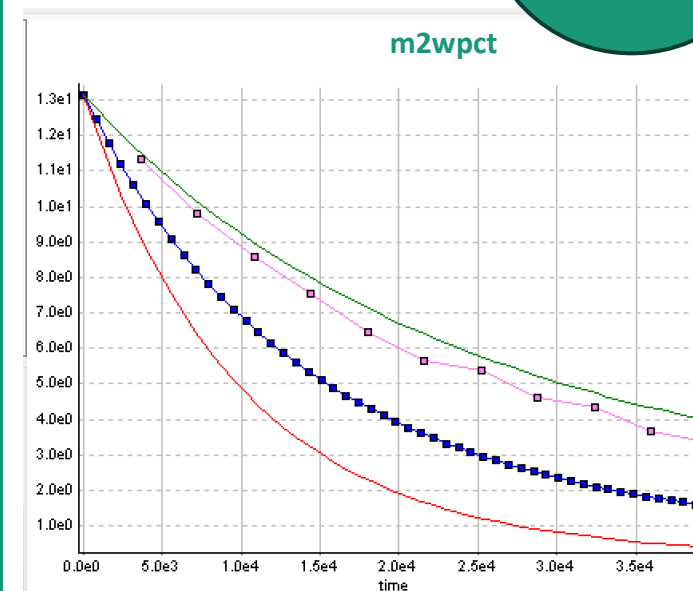
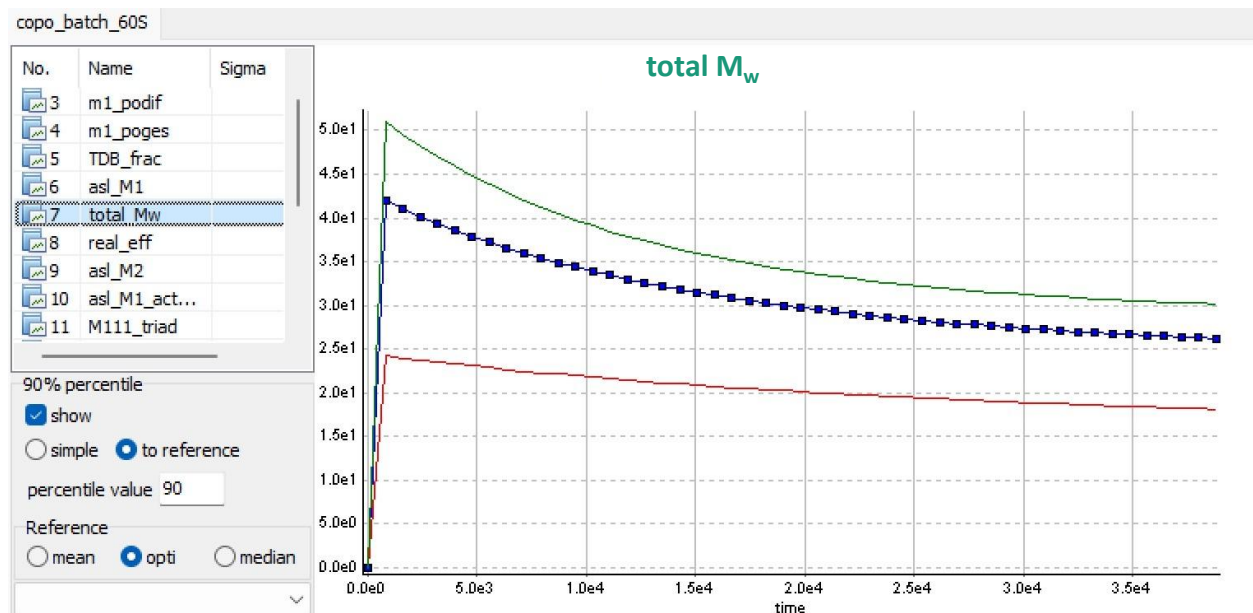
Sigma (rel.) use in variation Uncertainty in %

Gaussian prior 10 expected value (Langevin only)

Sensitivity analysis (cont.)

- ▶ Six parameters: $k_{p11}^f, k_{p22}^f, k_{t11}^f, k_{t22}^f, r_{12}, r_{21}$
- ▶ Initial values: 1000, 1000, $3 \cdot 10^8, 3 \cdot 10^8, 1, 1$
- ▶ Perturbation using normal distribution ($\sigma = 0.2$)
- ▶ Variation by σ -point method (only 13 required evaluations)

You can also already add data points



Perform
global search
(box,
simulated
annealing)

Global search: Simulated annealing

- ▶ Six parameters: $k_{p11}^f, k_{p22}^f, k_{t11}^f, k_{t22}^f, r_{12}, r_{21}$
- ▶ Initial values: 1000, 1000, $3 \cdot 10^8, 3 \cdot 10^8, 1, 1$
- ▶ 1000 evaluations with **1** and **3** batch experiments:
 $res_1 \approx 2.5\%$ and $res_3 \approx 12.5\%$

No.	Coefficient's name	Optimal value	Lower limit	Act. value	Upper limit	Coefficient's name	Optimal value
▶ 1	kp11.F	1.1254e+03	1.0000e+02	1.1935e+03	2.0000e+03	kp11.F	6.0915e+02
▶ 2	kp22.F	5.2120e+02	1.0000e+02	5.8454e+02	2.0000e+03	kp22.F	1.5902e+03
▶ 3	r12	1.1193e+00	1.0000e-01	1.5735e+00	3.0000e+00	r12	6.7286e-01
▶ 4	r21	1.6938e+00	1.0000e-01	1.8824e+00	3.0000e+00	r21	4.8649e-01
▶ 5	kt11.F	2.1586e+08	1.0000e+06	2.2553e+08	1.0000e+09	kt11.F	9.7250e+08
▶ 6	kt22.F	4.0907e+08	1.0000e+06	2.4811e+08	1.0000e+09	kt22.F	1.9605e+08

Residual

