

KINONE: a new software for the kinetic modelling of spectroscopic, calorimetric and concentration data

Julien Billeter, Yorck-Michael Neuhold and Konrad Hungerbühler

ETH Zurich, Institute for Chemical and Bioengineering, 8093 Zurich, Switzerland, E-mail: kinone@chem.ethz.ch



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Technology Group

Description of KINONE

What is KINONE?

KINONE is a piece of software dedicated to the kinetic modelling of spectroscopic, calorimetric and concentration data. It can be used in Simulation or in Fitting Mode. The interaction with KINONE is done through a Graphical User Interface.

Kinetic hard-modelling

KINONE can handle several kinetic models simultaneously. Kinetic reactions and thermodynamic equilibria can be entered in common chemical notation. Isothermal and non-isothermal expression for the model parameters are both possible.

Experimental conditions

Various experimental conditions are supported, such as batch (closed), semi-batch (flow in) or continuous (flow in and out), under isothermal or non-isothermal conditions.

Optimisation and fitting

Several kinetic problems comprised each by several data sets and models can be fitted sequentially, which makes KINONE suitable for the task of automatic model screening. A large choice of model and experimental parameters can be optimised.

Absorptivities and reaction enthalpies

In Simulation mode, the pure component spectra (molar absorptivities) and reaction enthalpies can be simulated. In Fitting mode, the pure component spectra and reaction enthalpies are calculated without calibration using a local or global analysis of multiple data sets. If some of the spectra and enthalpies are known, they can also be incorporated into the analysis.

Kinetic soft-modelling

KINONE contains several tools that help identifying the number of reactive species and elaborating plausible kinetic models, such as Principal Component Analysis (PCA), Evolving Factor Analysis (EFA) and Alternating Least Squares (ALS).

Pareto front

The Pareto-front, i.e. the sensitivity of signals to the weighting factors, can also be calculated.

Availability

KINONE is available for download free of charge as a Matlab (p-code) package or as an executable file.

Simulation using KINONE

An inhibited Michaelis-Menten mechanism

Spectroscopic and concentration data were simulated based on the reaction of dephosphorylation of fructose-1,6-bisphosphate (S) catalysed by fructose-1,6-bisphosphatase (E) leading to fructose-6-phosphate (P1) and inorganic phosphate (P2), in the presence of non-competitive inhibitor adenosine-5'-monophosphate (I). The kinetic model and the simulated data are shown in Figure 1 and Figure 2.

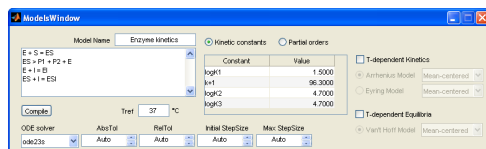


Figure 1
View of KINONE showing the kinetic model used for the simulation. Michaelis-Menten parameters: $v_{max,ref} = 0.14 \text{ mM min}^{-1}$, $K_M = 19.62 \text{ mM}$, $\alpha = 1.4$



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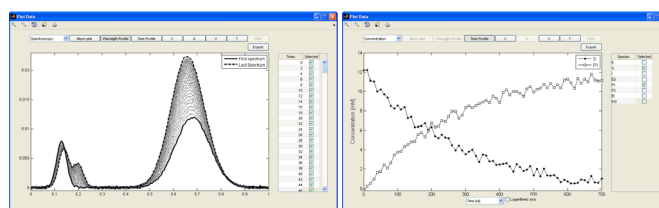
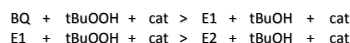


Figure 2
View of KINONE showing the simulated spectroscopic (left) and concentration (right) data. Initial conditions: $[E]_0 = 2.1 \mu\text{M}$, $[S]_0 = 12 \text{ mM}$ and $[I]_0 = 8.0 \mu\text{M}$, $V_0 = 300 \mu\text{L}$, $T_0 = 37^\circ\text{C}$.

Optimisation and fitting using KINONE

A consecutive epoxidation followed by mid-IR spectroscopy and calorimetry

The consecutive epoxidation of 2,5-di-tert-butyl-1,4-benzoquinone (BQ) with tert-butylhydroperoxide (tBuOOH) catalysed by Triton B (cat) was followed by mid-IR spectroscopy and by calorimetry, at four different temperatures. The following kinetic model was entered in KINONE:



A mean-centered Arrhenius expression of the model parameters at a reference temperature of 30°C was assumed.

The two signals were analysed together using weighting factors, 98.6% for spectroscopy and 1.4% for calorimetry, which balance the influence of the two analytical signals on all optimised model parameters ($k_{ref,1}$, $k_{ref,2}$, $E_{a,1}$ and $E_{a,2}$). Reaction enthalpies and pure component spectra were optimised globally. Species tBuOOH and tBuOH were set uncoloured as they could not be distinguished from species BQ, E1 and E2.

Optimised values for the four model parameters and for the two reaction enthalpies are close to literature values, as shown in Table 1. Optimised pure component spectra (not shown) are also close to the ones published in literature*.

Table 1
Optimised parameters and comparison with averaged literature values. Values in bracket are the ones obtained from the Pareto front in Figure 3.

	Reaction step	k_{ref} $\text{L}^2 \text{mol}^{-2} \text{min}^{-1}$	E_a kJ mol^{-1}	ΔH kJ mol^{-1}
This Work	1	13.3 ± 0.1 (11 ± 3)	60.2 ± 0.2 (61 ± 2)	-172 (-209)
	2	5.3 ± 0.1 (4 ± 2)	72.4 ± 0.5 (78 ± 5)	-185 (-167)
Literature*	1	17 ± 4	66 ± 7	-172 ± 18
	2	5 ± 2	71 ± 2	-190 ± 14

* Chemom. Intell. Lab. Syst., 85 (2007) 47; Chem. Eng. Sci., 59 (2004) 5795; J. Chem. Educ., 62 (1985) 175

The Pareto front obtained for this example is shown in Figure 3. The closest distance to the origin, which is often taken as the best compromise between the two signals, is achieved when the weighting factors are 90.3% and 9.7% for spectroscopy and calorimetry, respectively. Values for the model parameters and for the enthalpies at this point are given in Table 1 (values in brackets).

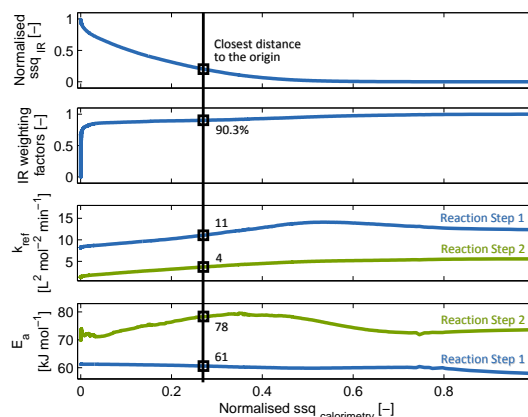


Figure 3
Pareto Front (top), values of the mid-IR weighting factors and model parameters at each Pareto point. The vertical line indicates the closest distance to the origin of the Pareto front and the values of the mid-IR weighting factors and model parameters at this point (see also Table 1, values in brackets).

