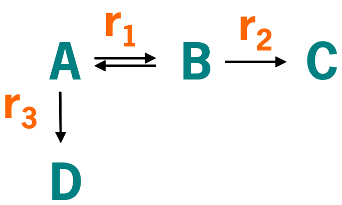
gPROMS Technologies

Model validation

State-of-the-art parameter estimation

Reaction scheme:



Reaction rates:

$$r_1 = \frac{k_1 K_A\left([A] - \frac{[B]}{K_{eq}}\right)}{1 + K_A[A] + K_B[B]}$$

$$r_2 = \frac{k_2 K_B [B]}{1 + K_A[A] + K_B[B]}$$

$$r_3 = \frac{k_3 K_A [A]}{1 + K_A[A] + K_B[B]}$$

$$k_i = k_i^0 \, e^{-\frac{E_i}{RT}}, \; i = 1, 2, 3$$

Source: Eurokin consortium
www.eurokin.org

A detailed gPROMS® process model is constructed from equations describing the physical and chemical phenomena that take place in the system. These equations usually involve *parameters* that can be adjusted to make the model predictions match observed reality.

Examples of model parameters include reaction kinetic constants, heat transfer coefficients, distillation stage efficiencies, constants within physical property correlations, and so on. For example, in the reaction scheme on the left, the rate equations for r_1, r_2 and r_3 depend on values of the Arrhenius parameters k_i^0 and E_i, the activation energy. The more accurate these parameters, the closer the model to reality.

Parameter estimation

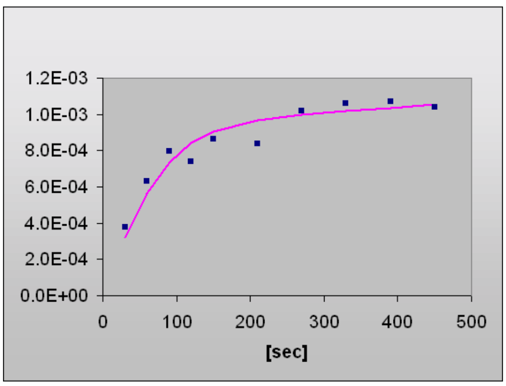
The process of fitting these parameters to laboratory or plant data is called *parameter estimation*. gPROMS contains powerful, state-of-the art parameter estimation capabilities that have been applied successfully to a wide range of problems. Key features are:

- Multiple parameters occurring in dynamic or steady-state models may be estimated simultaneously. Nonlinear models of arbitrary size and complexity – including multi-unit flowsheets – may be used.
- Data from both dynamic and steady-state experiments may be used.
- The results of the estimation are subjected to extensive statistical analysis.

Parameter estimation in gPROMS

gPROMS estimation techniques include **Least Squares** and the **Maximum Likelihood** formulation. The latter provides <u>simultaneous</u> estimation of parameters in both:

- the **physical model** of the process
- the **variance model** of the measuring instruments, which can be:
  - **constant variance** (e.g. a thermocouple with an accuracy of $\pm x$ K)
  - **constant relative variance** (e.g. a composition analyser with an error of $\pm x$ %)
  - **heteroscedastic variance**, combining both of the above.

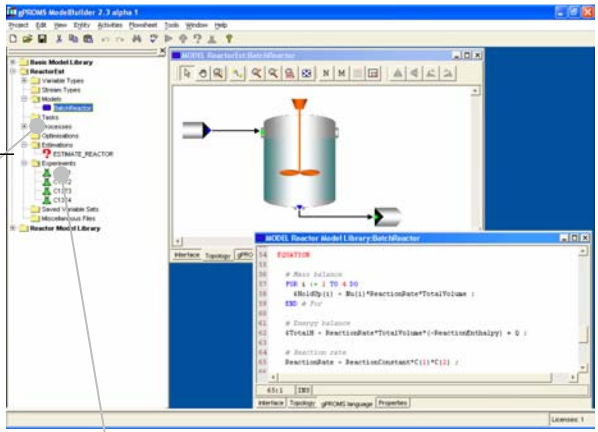


Detailed statistical analysis of results includes **residual** and **overlay plots** (right), **confidence ellipsoids**, **correlation matrix** and **model adequacy tests**.

The model company

Example

The example below shows how parameter estimation is performed in gPROMS to determine reaction kinetic constants.



Step 1

Construct a model of the process for which the measurements are being taken. Typically for reaction kinetics, this is a laboratory system which is small enough to ensure that extraneous effects – such as mixing phenomena – do not obscure the measurements. Of course, parameters can also be estimated from pilot plant or real plant data. This example uses a simple stirred-tank reactor.

Step 2

PARAMETER ESTIMATION BatchReactor:BatchReactor1_4

```
ESTIMATE
    Reactor.Ea(2)
    4.23014E+04 1.0E3 1.0E5

ESTIMATE
    Reactor.Ea(3)
    7.17235E+04 1.0E3  1.0E6

# Measured quantities and their variance models
MEASURE
    REACTOR.CON(1)
    HETEROSCEDASTIC (0.1 : 1.0E-4 : 1.0; 0.5 : 0.0 : 1.0)
```

Define the parameters to be estimated and the **variance model** to be used **for each measuring instrument**. In this example, the heteroscedastic variance model is selected for the composition analysers, meaning that gPROMS will determine automatically the optimal proportion of constant and relative variance to be taken into account.

EXPERIMENT BatchReactor:BATCH_1

```
    REACTOR.CON(1) 0.65
    REACTOR.CON(3) 0.00
    REACTOR.CON(4) 0.00

MEASURE
    REACTOR.CON(1)
    30   3.97E-01
    60   2.60E-01
    90   1.56E-01
    120  9.10E-02
    150  4.84E-02
    210  1.98E-02
```

Step 3

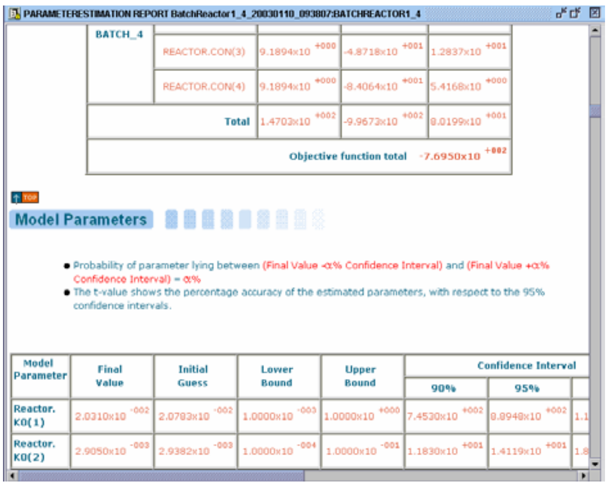
Enter the **experimental data sets**. You may include as many experiments as required, and these may contain steady-state or dynamic data sets.

Step 4

Execute the estimation run.

Step 5

Check the results in the detailed analysis (left) and the confidence ellipsoid plots (right).



PARAMETERESTIMATION REPORT BatchReactor1_4_20030110_093807:BATCHREACTOR1_4

BATCH_4	REACTOR.CON(3)	$9.1894\times10^{+000}$	$-4.8718\times10^{+001}$	$1.2837\times10^{+001}$
	REACTOR.CON(4)	$9.1894\times10^{+000}$	$-8.4064\times10^{+001}$	$5.4168\times10^{+000}$
	Total	$1.4703\times10^{+002}$	$-9.9673\times10^{+002}$	$8.0199\times10^{+001}$
	Objective function total			$-7.6950\times10^{+002}$

Model Parameters

- Probability of parameter lying between (Final Value -α% Confidence Interval) and (Final Value +α% Confidence Interval) = α%
- The t-value shows the percentage accuracy of the estimated parameters, with respect to the 95% confidence intervals.

Model Parameter	Final Value	Initial Guess	Lower Bound	Upper Bound	Confidence Interval 90%	95%	
Reactor. K0(1)	2.0310×10^{-002}	2.0783×10^{-002}	1.0000×10^{-003}	$1.0000\times10^{+000}$	$7.4530\times10^{+002}$	$8.8948\times10^{+002}$	1.1
Reactor. K0(2)	2.9050×10^{-003}	2.9382×10^{-003}	1.0000×10^{-004}	1.0000×10^{-001}	$1.1830\times10^{+001}$	$1.4119\times10^{+001}$	1.8