

SteadyFit

A program for the determination of kinetic and thermodynamic constants in completely mixed flow-through systems at steady state

Manual

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by

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1 Introduction

Natural systems are usually not closed but open. Therefore, they are better represented by a steady-state approach than by an equilibrium approach. On a molecular, mechanistic level, the prediction of the chemical speciation in systems at steady state requires (i) definition of the system boundaries, (ii) the selection of all relevant chemical species occurring within the system and crossing the system boundaries, (iii) the determination of the mean residence time of the species in the system, (iv) the determination of the reactions the species are involved in and (v) the assignment of the reactions to fast and slow processes with respect to the mean residence time. For all processes, reaction stoichiometries must be known. Fast processes are assumed to be at equilibrium and require knowledge of thermodynamic constants. Slow processes are described by rate laws which include kinetic constants. If all the information required is available, the program *STEADYQL* ([1], [2]) can be used to calculate the speciation of the system at steady state. *STEADYQL* provides a completely general algebraic framework with which the chemical speciation of a flow-through system where fluxes into and out of it are balanced can easily be computed. It is not restricted to homogeneous systems, but can also handle heterogeneous systems and thus include reactions at the solid-water interface (e.g. dissolution of minerals, surface catalysed hydrolysis of pesticides). Unknown thermodynamic constants can be determined from batch experiments, using e.g. the program *FITEQL* ([8]). Unknown kinetic constants can also be determined from batch experiments. However, long-term effects (e.g. blocking of reactive surface sites by adsorption of products) can usually not be observed, since the amount of educts is limited. For the evaluation of rate equations and the determination of rate constants from experiments with completely mixed flow-through reactors, the program *SteadyFit* has been developed ([3]). This manual describes the use of the program *SteadyFit*.

1.1 Contents of this manual

We assume that the general framework of *STEADYQL* is known and advice the reader to first read the papers [1], [2] and [3] before using *SteadyFit*. The use of *STEADYQL* has also been described in a manual ([10]). Since *STEADYQL* is based on *MICROQL* ([7], [9]), experience with *MICROQL* is advantageous.

After a brief description of the general features of *SteadyFit*, we will mainly focus on the different input file formats, using as an example the system described in [2]. The glossary at the end of this manual lists most of the terms used in the *STEADYQL* and *SteadyFit* framework.

1.2 Program description

The program and documentation can be obtained from

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The files distributed are not listed in detail in this manual, since the distribution might vary with time. Basically, you can expect one or more executable files (optimized for different processors) and all example input and output files described in this manual. A complete list of files is contained in the file *README.1ST*, including a detailed installation description – which might not be more than copying the files to a directory on the hard disk.

SteadyFit runs presently only on DOS machines and is called from the DOS command line with *SFTxxx inputfile [outputfile]* (where xxx is the processor abbreviation, which is one of 86, 87, 286, 287, 386, 387, 486, 487 where *86 denotes coprocessor emulation and *87 optimization for the specified coprocessor). If *outputfile* is not specified, the name of the inputfile is taken and its extension is changed to *out*. During most calculations, the program can be interrupted by pressing any key.

The number of species, components, processes etc. is restricted. Type `SFTxxx help` to obtain the maximum number of components, species, etc. and the length of names supported (printed to the file `sft_help.txt`).

2 Calculation Types

SteadyFit can perform different types of calculations. They are controlled by the control parameter *CalcType* which can take the following values¹:

<i>CalcType</i>	Explanation
1	Single steady-state calculation, including analytical sensitivity analysis for all equilibrium constants and parameters of the slow processes
2	Multiple steady-state calculation with a series of one or more independent variables (x variables, unlimited number of datapoints)
3	Fitting kinetic and thermodynamic constants to a set of experimental data (<i>SteadyFit</i>)
4	Multiple steady-state calculation for numerical sensitivity analysis of the system. All equilibrium constants and parameters of the slow processes are – one after the other – varied between a minimal and a maximal value (specified by minimal and maximal factors in the input file). If model 1 (Constant Capacitance) is used, also the capacitance and the surface site density are varied in the range given.
5	Multiple steady-state calculation to evaluate the weighted sum of squared residuals between the measured and calculated dependent variables, χ^2 (the merit function in the Levenberg-Marquardt routine, see [4]) as a function of the parameters to be fitted. Use this to see whether there is a (global) minimum around the first guess values of the parameters to be optimised before running <i>SteadyFit</i> (i.e. <i>CalcType</i> = 3).

Except for *CalcType* = 3, all calculations are essentially *STEADYQL* calculations.

¹Note: the sequence of *CalcType* values is not given by logical criteria but is a result of the development of the program.

3 Models

Presently, two models are supported:

Model	Explanation
0	Solution speciation (no surface complexation model)
1	Constant Capacitance Model by Schindler and Stumm ([5])

4 Input file format

The input file for *SteadyFit* is organized in blocks. Every block except the title block starts with one or more comment lines. The comments usually contain a brief description of the contents of a block. Some blocks are optional, depending on the model and the calculation type. In Table 1, an overview of the different blocks is given. Numbers in brackets are the number of lines for the entry in the block. The following symbols are used: I = total number of species, K = total number of components, L = number of processes, P = number of parameters, n = number of serial data. The *condition* is given for optional blocks, no condition means that the specified block appears in all types of input files. Examples of input files for different types of calculations are given in Chapter 6.

Table 1: Overview of input file structure

Block	Condition	# Lines	Contents
Title		(2)	title
		(1)	comment
1		(1)	comment
		(1)	control parameters
2	Model=1	(2)	comment
		(1)	model 1 parameters
3	Model=1	(1)	comment
		(1)	model 1 parameters
4		(1)	comment
		(1)	total number of species and components, number of components with fixed activity
5		(1)	comment
		(1)	number of immobile species, number of immobile components
6		(1)	comment
		(1)	number of processes, number of parameters
7		(2)	comment
		(1)	names of species, species concentration used as Y-variable (Y/-), logK fitted (*/-), logK values, A-matrix, printout control
8		(2)	comment
		(K)	names of new components, components total concentration used as y-variable (Y/-), L-matrix, log X, total concentration, charge, printout control
9		(2)	comment
		(L)	description and names of slow processes
10		(2)	comment
		(I)	names of species, F matrix
11		(2)	comment
		(1)	RT vector
12		(2)	comment
		(I)	names of species, N matrix
13		(2)	comment
		(P)	names of parameters, W matrix (also called Q-matrix)
14		(2)	comment
		(P)	names of parameters, parameter used as x-variable (X/-), parameter fitted (*/-), parameter value
15	<i>CalcType</i> = 2	(1)	comment
		(1)	number of serial data points
16	<i>CalcType</i> = 2	(1)	comment
		(n)	x data
17	<i>CalcType</i> = 3	(1)	comment
		(1)	number of serial (experimental) data
18	<i>CalcType</i> = 3	(1)	comment
		(n)	x, y, σ_{rel} , σ_{abs} of serial data
19	<i>CalcType</i> = 4	(1)	comment
		(1)	number of serial data
20	<i>CalcType</i> = 4	(1)	comment
		(1)	minimum and maximum factor for sensitivity plot
21	<i>CalcType</i> = 5	(1)	comment
		(1)	number of data points per equilibrium constant or parameter investigated
22	<i>CalcType</i> = 5	(1)	comment
		(1)	minimum and maximum factor for χ^2 plot

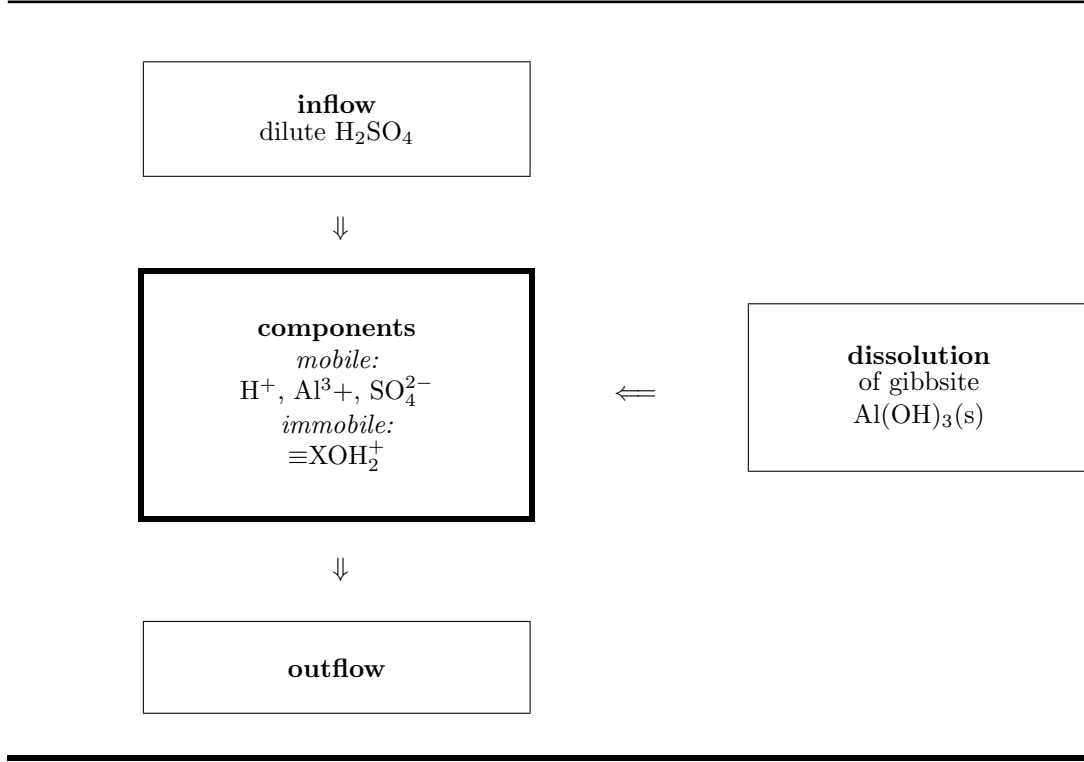
I = total number of species, K = total number of components, L = number of processes, P = number of parameters, n = number of serial data

5 Example

The example deals with the proton-induced dissolution of gibbsite, $\text{Al}(\text{OH})_3(\text{s})$ as described in [2].

We define a box in which gibbsite is percolated by dilute sulfuric acid (Figure 1). This results in the dissolution of gibbsite and an increase in pH. The reaction solution is constantly removed from the box. After steady state is reached, the species' concentration in the box remains stable.

Figure 1: The dissolution of gibbsite. Equilibrium reactions: box with bold frame; sources (inflow, dissolution) and sinks (outflow): other boxes.



There are 9 mobile species, namely H^+ , OH^- , SO_4^{2-} , Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3^0$, $\text{Al}(\text{OH})_4^-$, AlSO_4^+ and three immobile species, namely XOH_2^+ , XOH and XSO_4^- .

From the set of species we select three mobile components (H^+ , SO_4^{2-} , Al^{3+}) and one immobile component (XOH_2^+) with which we can represent every species through equilibrium reactions. Table 2 shows the **A** matrix which contains this information in the form used by the program and the **logK** vector which contains the logarithmic values of the equilibrium constants.

In the system there are two slow processes, the inflow of dilute sulfuric acid from an infinite reservoir, inH_2SO_4 , and the dissolution of gibbsite, disGib . The back reaction of the dissolution is neglected under the assumption that the system is strongly undersaturated.

Every process is characterised by a reaction equation and a rate equation which does not take a negative sign. Increase and decrease of the species' concentration are described by the sign of their stoichiometric coefficients.

The first process (inH_2SO_4) describes the inflow of H^+ (concentration $2c$) and SO_4^{2-} (concentration c). The stoichiometric coefficients of the protons and the sulfate anion are contained in the **F** matrix (Table 3). The process is described by the rate equation

$$R_1 = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{1}{2} \frac{d[\text{H}^+]}{dt} = vc \quad (1)$$

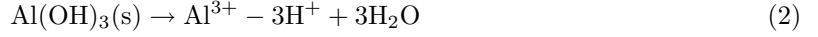
where R_1 = rate ($\text{mol dm}^{-2} \text{s}^{-1}$), v = flow velocity (dm s^{-1}) and c = concentration of H_2SO_4 (mol dm^{-3}). The value of the flow velocity v corresponds to a certain annual net precipitation. v and c are

Table 2: The **A** matrix describes the formation of the species from the components. The equilibrium constants for every reaction are listed in the **logK** vector.

Species i	Component j				logK
	XOH ₂ ⁺	H ⁺	SO ₄ ²⁻	Al ³⁺	
H ⁺	0	1	0	0	0.0
OH ⁻	0	-1	0	0	-14.0
SO ₄ ²⁻	0	0	1	0	0.0
Al ³⁺	0	0	0	1	0.0
AlOH ²⁺	0	-1	0	1	-5.0
Al(OH) ₂ ⁺	0	-2	0	1	-10.1
Al(OH) ₃ ⁰	0	-3	0	1	-16.0
Al(OH) ₄ ⁻	0	-4	0	1	-23.0
AlSO ₄ ⁺	0	0	1	1	3.2
XOH ₂ ⁺	1	0	0	0	0.0
XOH ⁻	1	-1	0	0	-7.5
XSO ₄ ⁻	1	0	1	0	4.5

the first two process parameters (v must always be the first in the list!). There is an infinite reservoir of H₂SO₄ and since H₂SO₄ is a strong acid, it dissociates completely.

The second process (*disGib*) describes the dissolution of gibbsite according to



Again, the stoichiometric coefficients are contained in the **F** matrix. This process can be described using the following empirical rate equation ([6]):

$$R_2 = \frac{d[\text{Al}^{3+}]}{dt} = \frac{1}{3} \frac{d[\text{H}^+]}{dt} = k[\text{H}^+]^{0.4} \quad (3)$$

The rate constant k (units defined by Equation 3), is the third process parameter. Its exponent in Equation 3 is 1 and listed in the **W** matrix (Table 4). The rate R_2 depends on the hydronium ion concentration, $[\text{H}^+]$, contrary to the rate describing process *inH₂SO₄*. The exponent of $[\text{H}^+]$, 0.4, is an element of the **N** matrix (Table 5). It is assumed that the gibbsite surface doesn't change during the time span considered. Thus, the reacting surface is constant and treated as an implicit factor in the rate constant.

Table 3: The elements of the \mathbf{F} matrix correspond to the stoichiometric coefficients of the species in the reaction equations of the slow processes.

Species i	Process l	
	inH_2SO_4	$disGib$
H^+	2	-3
OH^-	0	0
SO_4^{2-}	1	0
Al^{3+}	0	1
$AlOH^{2+}$	0	0
$Al(OH)_2^+$	0	0
$Al(OH)_3^0$	0	0
$Al(OH)_4^-$	0	0
$AlSO_4^+$	0	0
XOH_2^-	0	0
XOH	0	0
XSO_4^-	0	0

Table 4: The elements of the \mathbf{W} matrix are the exponents of the parameter in the rate equations. (Note: the flow velocity v must always be the first parameter in the list.)

Parameter m	Process l	
	inH_2SO_4	$disGib$
v	1	0
c	1	0
k	0	1

Table 5: The exponents of the species' concentrations in the rate equations are the elements of the **N** matrix.

Species i	Process l	
	inH_2SO_4	$disGib$
H^+	0	0.4
OH^-	0	0
SO_4^{2-}	0	0
Al^{3+}	0	0
$AlOH^{2+}$	0	0
$Al(OH)_2^+$	0	0
$Al(OH)_3^0$	0	0
$Al(OH)_4^-$	0	0
$AlSO_4^+$	0	0
XOH_2^+	0	0
XOH	0	0
XSO_4^-	0	0

6 Sample calculations

In the following sections, commented input files (extension **dat**) and some output files (extension **out**) and graphs are presented. These files are part of the *SteadyFit* package. The input files listed here contain comments. They are printed like this

■ this is a comment ■

and are not part of the input file. The sample calculations are all based on the example discussed in the previous chapter. The character “#” means “number”. The parameter *output* is explained in the glossary.

6.1 Single steady-state calculation ($CalcType = 1$)

This is the 'classical' *STEADYQL* calculation and corresponds to the calculation presented in [2]. Its calculation type input variable *CalcType* is 1.

Listing of gibs1.dat:

Weathering of Gibbsite: Furrer et al. (1989), Geochim. Cosmochim. Acta, 53, 595-601
Rate law: $r=k\{XOH_2^+\}$, $k=1.4E-10$

=====

- (1) calculation type; model; maximum no of iterations; epsilon; output
1 0 35 1.E-10 3

■ If the *maximum no of iterations* is exceeded in the *STEADYQL* or the Levenberg-Marquardt subroutines, the calculation is terminated. *epsilon* is the convergence criterion for the *STEADYQL* subroutine.
■

- (4) total # of species; total # of components; # of comp. with fixed activity
12 4 0

- (5) # of immobile species; # of immobile components
3 1

- (6) # of processes; # of parameters
2 3

- (7) names of species; Y/-; */-; logK; A-matrix; print
- Y/- */- log K XOH2+ Al3+ SO4-2 H+ print

H+	-	-	0.0	0	0	0	+1	T
OH-	-	-	-14.0	0	0	0	-1	T
SO4-2	-	-	0.0	0	0	+1	0	T
Al+3	-	-	0.0	0	+1	0	0	T
Al(OH)+2	-	-	-5.0	0	+1	0	-1	T
Al(OH)2+	-	-	-10.1	0	+1	0	-2	T
Al(OH)3	-	-	-16.0	0	+1	0	-3	T
Al(OH)4-	-	-	-23.0	0	+1	0	-4	T
AlSO4+	-	-	3.2	0	+1	+1	0	T
XOH2+	-	-	0.0	+1	0	0	0	T
XOH	-	-	-7.5	+1	0	0	-1	T
XSO4-	-	-	4.5	+1	0	+1	0	T

■ Columns Y/- and */- are not used in *CalcType* = 1 calculations. Nevertheless, a '-' must be specified. Remember that the sequence of components and species is important (see Glossary): first immobile, then mobile components and at the end components with fixed activity, species must be listed in the order mobile and then immobile. The column *print* controls whether the concentration of a species is printed for calculations resulting in series (T=TRUE, F=FALSE). ■

```
- (8) names of new components; X/Y/-; L-matrix; logX; T; charge; print
-n\o      X/Y/-      XOH2+      Al3+      SO4-2      H+      log X      Total Charge print
XOH2+      -          +1          0          0          0          -6      1E-4      +1      T
Al+3        -          0          +1          0          0          -6          0      +3      T
SO4-2        -          0          0          +1          0          -6          0      -2      T
H+           -          0          0          0          +1          -6          0      +1      T
```

■ The column X/Y/- is not used in *CalcType* = 1, specify a '-'. The *L matrix* is used to transform an old set of components to a new set. If no transformation is necessary, specify the unity matrix. The *charge* is for control purposes only (see output file). The column *print* controls whether the total concentration of a component is printed for calculations resulting in series (T=TRUE, F=FALSE). ■

```
- (9) slow processes
- description of processes; names of processes
inflow_of_solution      inflow
dissolution_of_Al(OH)3   dissol
```

■ The description of processes is only used in the input file (they must be specified). Note that no spaces should be used to separate words, use the underscore character instead. ■

```
-(10) names of species; F-matrix: stoichiometry of species i in process 1
-      inflow      dissol
H+      +2          0
OH-      0          +3
SO4-2     +1          0
Al+3       0          +1
Al(OH)+2   0          0
Al(OH)2+   0          0
Al(OH)3     0          0
Al(OH)4-    0          0
AlSO4+      0          0
XOH2+       0          0
XOH         0          0
XSO4-       0          0
- (11) RT[l] type of rate equation: 0 order (0), 1st order (1), power law (2)
-      inflow      dissol
      0          2
```

■ Consult the glossary for the definition of *RT*. ■

```
- (12) names of species; N-matrix: power of species i in process 1
-      inflow      dissol
H+      0          +0.4
OH-      0          0
SO4-2     0          0
Al+3       0          0
Al(OH)+2   0          0
Al(OH)2+   0          0
Al(OH)3     0          0
Al(OH)4-    0          0
AlSO4+      0          0
XOH2+       0          0
XOH         0          0
```

```

XS04-      0      0
- (13) names of parameters (v FIRST); W-matrix: power of parameter m in process 1
-      inflow  dissol
v      +1      0
c      +1      0
k      0      +1

```

■ The flow velocity v must be the first parameter in the list! ■

```

- (14) names of parameters; X/-; */-; P: parameter values (units: mol, dm, s)
- FIRST parameter flow velocity v
v      -      -      3.17E-07
c      -      -      5.00E-05
k      -      -      1.4E-10

```

■ The columns $X/-$ and $*/-$ are not used in $CalcType = 1$. Specify a '-'. ■

Listing of gibs1.out:

Problem title:

Weathering of Gibbsite: Furrer et al. (1989), Geochim. Cosmochim. Acta, 53, 595-601

Rate law: $r=k\{XOH2+\}$, $k=1.4E-10$

Input file:

GIBS1.DAT

Input data for verification

=====

Components:

=====

```
- mobile : 3
  Al+3, SO4-2, H+
- immobile : 1
  XOH2+
```

Number of components with fixed activity : 0

Species :

=====

```
- mobile : 9
  H+, OH-, SO4-2, Al+3, Al(OH)+2, Al(OH)2+, Al(OH)3,
  Al(OH)4-, AlSO4+
- immobile : 3
  XOH2+, XOH, XS04-
```

Mass-action equations:

=====

```
[H+]          = 10^ 0.000 [H+]
[OH-]          = 10^-14.00 [H+]^(-1.)
[SO4-2]        = 10^ 0.000 [SO4-2]
[Al+3]         = 10^ 0.000 [Al+3]
[Al(OH)+2]     = 10^-5.000 [Al+3] [H+]^(-1.)
[Al(OH)2+]     = 10^-10.10 [Al+3] [H+]^(-2.)
[Al(OH)3]      = 10^-16.00 [Al+3] [H+]^(-3.)
[Al(OH)4-]     = 10^-23.00 [Al+3] [H+]^(-4.)
[AlSO4+]       = 10^ 3.200 [Al+3] [SO4-2]
[XOH2+]        = 10^ 0.000 [XOH2+]
[XOH]          = 10^-7.500 [XOH2+] [H+]^(-1.)
[XS04-]        = 10^ 4.500 [XOH2+] [SO4-2]
```

Processes:

=====

Number : 2

```
inflow      : R1  = v c
dissol      : R2  = k [H+]^ 0.400
```

Parameters:

=====

Number : 3

Values :

```
v      : 3.170E-07
c      : 5.000E-05
k      : 1.400E-10
```

S[l,j] for mobile components

=====

```
1  id          Al+3      SO4-2      H+      Charge balance
```

1	inflow	0.	1.	2.	0.0
2	dissol	1.	0.	-3.	0.0

The program converged after 9 iterations.

The results at steady state are:

a) chemical speciation

i	id	logC	C
1	H+	-4.142	7.214E-05
2	OH-	-9.858	1.386E-10
3	SO4-2	-4.306	4.938E-05
4	Al+3	-5.102	7.899E-06
5	Al(OH)+2	-5.961	1.095E-06
6	Al(OH)2+	-6.919	1.206E-07
7	Al(OH)3	-8.677	2.104E-09
8	Al(OH)4-	-11.54	2.917E-12
9	AlSO4+	-6.209	6.182E-07
10	XOH2+	-4.409	3.903E-05
11	XOH	-7.767	1.711E-08
12	XSO4-	-4.215	6.095E-05

j	id	logX	X	T	Y
1	XOH2+	-4.409	3.903E-05	1.000E-04	-2.582E-18
2	Al+3	-5.102	7.899E-06	9.735E-06	6.059E-17
3	SO4-2	-4.306	4.938E-05	5.000E-05	-2.780E-18
4	H+	-4.142	7.214E-05	7.080E-05	-8.819E-17

b) volume specific fluxes (in mol dm⁻³ s⁻¹)

j	id	Al+3	SO4-2	H+
1	inflow	0.000E+00	1.585E-11	3.170E-11
2	dissol	3.086E-12	0.000E+00	-9.258E-12
	outflow	-3.086E-12	-1.585E-11	-2.244E-11

c) normalized sensitivity coefficients, dlnC[i]/dlnP[m])

i	id	v	c	k
1	H+	3.290E-01	1.180E+00	-3.290E-01
2	OH-	-3.290E-01	-1.180E+00	3.290E-01
3	SO4-2	1.018E-02	9.929E-01	-1.018E-02
4	Al+3	-8.237E-01	5.715E-01	8.237E-01
5	Al(OH)+2	-1.153E+00	-6.082E-01	1.153E+00
6	Al(OH)2+	-1.482E+00	-1.788E+00	1.482E+00
7	Al(OH)3	-1.811E+00	-2.968E+00	1.811E+00
8	Al(OH)4-	-2.140E+00	-4.147E+00	2.140E+00
9	AlSO4+	-8.135E-01	1.564E+00	8.135E-01
10	XOH2+	-6.151E-03	-6.050E-01	6.151E-03
11	XOH	-3.351E-01	-1.785E+00	3.351E-01
12	XSO4-	4.033E-03	3.879E-01	-4.033E-03

d) normalized sensitivity coefficients, dlnC[i]/dlnK[ii])
(species in rows, constants in columns)

i	id	H+	OH-	SO4-2	Al+3	Al(OH)+2	Al(OH)2+	Al(OH)3
1	H+	1.666E-02	1.637E-06	9.949E-04	-1.287E-02	1.114E-02	2.651E-03	7.111E-05
2	OH-	9.833E-01	1.000E+00	-9.949E-04	1.287E-02	-1.114E-02	-2.651E-03	-7.111E-05
3	SO4-2	1.596E-03	-1.089E-08	1.158E-02	1.013E-02	1.318E-03	1.356E-04	2.201E-06
4	Al+3	-1.290E-01	8.811E-07	6.330E-02	1.810E-01	-1.066E-01	-1.097E-02	-1.780E-04
5	Al(OH)+2	8.543E-01	-7.557E-07	6.231E-02	-8.061E-01	8.823E-01	-1.362E-02	-2.491E-04
6	Al(OH)2+	1.838E+00	-2.392E-06	6.131E-02	-7.932E-01	-1.289E-01	9.837E-01	-3.203E-04
7	Al(OH)3	2.821E+00	-4.029E-06	6.032E-02	-7.804E-01	-1.400E-01	-1.892E-02	1.000E+00
8	Al(OH)4-	3.804E+00	-5.666E-06	5.932E-02	-7.675E-01	-1.511E-01	-2.157E-02	-4.625E-04
9	AlSO4+	-1.274E-01	8.702E-07	-9.251E-01	-8.089E-01	-1.053E-01	-1.083E-02	-1.758E-04
10	XOH2+	-1.141E-03	6.920E-09	6.025E-01	-6.174E-03	-8.012E-04	-8.221E-05	-1.330E-06
11	XOH	9.822E-01	-1.630E-06	6.015E-01	6.697E-03	-1.195E-02	-2.733E-03	-7.244E-05

12	XS04-	4.548E-04	-3.974E-09	-3.860E-01	3.952E-03	5.164E-04	5.341E-05	8.718E-07
----	-------	-----------	------------	------------	-----------	-----------	-----------	-----------

i	id	Al(OH)4-	AlSO4+	XOH2+	XOH	XS04-
1	H+	1.330E-07	-9.949E-04	0.000E+00	0.000E+00	0.000E+00
2	OH-	-1.330E-07	9.949E-04	0.000E+00	0.000E+00	0.000E+00
3	S04-2	2.822E-09	-1.158E-02	0.000E+00	0.000E+00	0.000E+00
4	Al+3	-2.283E-07	-6.330E-02	0.000E+00	0.000E+00	0.000E+00
5	Al(OH)+2	-3.613E-07	-6.231E-02	0.000E+00	0.000E+00	0.000E+00
6	Al(OH)2+	-4.943E-07	-6.131E-02	0.000E+00	0.000E+00	0.000E+00
7	Al(OH)3	-6.273E-07	-6.032E-02	0.000E+00	0.000E+00	0.000E+00
8	Al(OH)4-	1.000E+00	-5.932E-02	0.000E+00	0.000E+00	0.000E+00
9	AlSO4+	-2.254E-07	9.251E-01	0.000E+00	0.000E+00	0.000E+00
10	XOH2+	-1.698E-09	7.059E-03	6.097E-01	-1.711E-04	-6.095E-01
11	XOH	-1.347E-07	8.054E-03	-3.903E-01	1.000E+00	-6.095E-01
12	XS04-	1.125E-09	-4.523E-03	-3.903E-01	-1.711E-04	3.905E-01

e) normalized sensitivity coefficients, $d\ln T[j]/d\ln P[m]$)

j	id	v	c	k
1	XOH2+	0.000E+00	0.000E+00	0.000E+00
2	Al+3	-8.684E-01	4.719E-01	8.684E-01
3	S04-2	-5.959E-14	1.000E+00	5.959E-14
4	H+	3.582E-01	1.218E+00	-3.582E-01

f) normalized sensitivity coefficients, $d\ln T[j]/d\ln K[\alpha]$)

j	id	H+	OH-	S04-2	Al+3	Al(OH)+2	Al(OH)2+	Al(OH)3
1	XOH2+	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
2	Al+3	6.665E-03	6.547E-07	3.980E-04	-5.149E-03	4.458E-03	1.060E-03	2.844E-05
3	S04-2	-9.337E-15	6.375E-20	1.293E-13	-5.925E-14	-7.710E-15	-7.936E-16	-1.288E-17
4	H+	-2.749E-03	-2.701E-07	-1.642E-04	2.124E-03	-1.839E-03	-4.374E-04	-1.173E-05

j	id	Al(OH)4-	AlSO4+	XOH2+	XOH	XS04-
1	XOH2+	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
2	Al+3	5.320E-08	-3.980E-04	0.000E+00	0.000E+00	0.000E+00
3	S04-2	-1.652E-20	-3.019E-15	0.000E+00	0.000E+00	0.000E+00
4	H+	-2.195E-08	1.642E-04	0.000E+00	0.000E+00	0.000E+00

6.2 Multiple steady-state calculation ($CalcType = 2$)

Often, one needs to perform a whole series of calculations where one or several parameter values, e.g. the flow velocity v , are varied over a specific range. This type of calculation has $CalcType = 2$. Any independent variable can be used in that sort of calculation with *SteadyFit*. As explained in the input file listed below, the character “X” can be specified in the appropriate places and the values are appended at the end of the file.

Listing of gibs2.dat:

Weathering of Gibbsite: Furrer et al. (1989), Geochim. Cosmochim. Acta, 53, 595-601
Rate law: $r=k\{XOH2+\}$; range over v

```
=====
- (1) calculation type; model; maximum no of iterations; epsilon; output
  2 0 35 1.E-10 33
- (4) total # of species; total # of components; # of comp. with fixed activity
  12 4 0
- (5) # of immobile species; # of immobile components
  3 1
- (6) # of processes; # of parameters
  2 3
- (7) names of species; Y/-; */-; logK; A-matrix; print
-
  Y/-      */-      log K   XOH2+   Al3+   SO4-2   H+   print
H+         -       -       0.0      0      0      0   +1   T
OH-        -       -      -14.0     0      0      0   -1   T
SO4-2      -       -       0.0      0      0     +1    0   T
Al+3       -       -       0.0      0     +1      0    0   T
Al(OH)+2   -       -      -5.0      0     +1      0   -1   T
Al(OH)2+   -       -     -10.1      0     +1      0   -2   T
Al(OH)3     -       -     -16.0      0     +1      0   -3   T
Al(OH)4-    -       -     -23.0      0     +1      0   -4   T
AlSO4+      -       -       3.2      0     +1     +1    0   T
XOH2+       -       -       0.0     +1      0      0    0   T
XOH         -       -      -7.5     +1      0      0   -1   T
XSO4-       -       -       4.5     +1      0     +1    0   T
- (8) names of new components; Y/-; L-matrix; logX; T; charge; print
-n\o      X/Y/-      XOH2+   Al3+   SO4-2   H+   log X   Total Charge print
XOH2+     -          +1      0      0      0   -6   1E-4   +1   T
Al+3      -          0      +1      0      0   -6      0   +3   T
SO4-2     -          0      0     +1      0   -6      0   -2   T
H+        -          0      0      0     +1   -6      0   +1   T
- (9) slow processes
- description of processes; names of processes
  inflow_of_solution      inflow
  dissolution_of_Al(OH)3   dissol
- (10) names of species; F-matrix: stoichiometry of species i in process 1
-
  inflow  dissol
H+       +2      0
OH-       0     +3
SO4-2    +1      0
Al+3      0     +1
Al(OH)+2  0      0
Al(OH)2+  0      0
Al(OH)3   0      0
Al(OH)4-  0      0
AlSO4+    0      0
XOH2+     0      0
XOH        0      0
XSO4-     0      0
- (11) RT[l] type of rate equation: 0 order (0), 1st order (1), power law (2)
-
  inflow  dissol
  0       2
- (12) names of species; N-matrix: power of species i in process 1
-
  inflow  dissol
H+       0     +0.4
OH-       0      0
SO4-2     0      0
Al+3      0      0
```

Al(OH)+2	0	0
Al(OH)2+	0	0
Al(OH)3	0	0
Al(OH)4-	0	0
AlSO4+	0	0
XOH2+	0	0
XOH	0	0
XSO4-	0	0

- (13) names of parameters (v FIRST); W-matrix: power of parameter m in process 1

	inflow	dissol
v	+1	0
c	+1	0
k	0	+1

- (14) names of parameters; X/-; */-; P: parameter values (units: mol, dm, s)

- FIRST parameter flow velocity v

v	X	-	3.17E-07
c	-	-	5.00E-05
k	-	-	1.4E-10

■ The X in the column X/- signifies that x serial data is provided for the parameter v (flow velocity). ■

- (17) # of serial datapoints
21

■ 21 datapoints need to be calculated with varying values of v as specified in the next block. ■

- (18) serial data (v)

1.58E-07
1.74E-07
1.90E-07
2.06E-07
2.22E-07
2.38E-07
2.54E-07
2.69E-07
2.85E-07
3.01E-07
3.17E-07
3.33E-07
3.49E-07
3.65E-07
3.80E-07
3.96E-07
4.12E-07
4.28E-07
4.44E-07
4.60E-07
4.75E-07

■ The serial data for the flow velocity v is provided here. Note that if there are several x-variables, the data must be listed in columns in the same sequence as the "X"'s appear above. For *CalcType* = 2, there is no limit on the number of data points that can be input. ■

6.3 Surface complexation using the Constant Capacitance Model

SteadyFit implements the Constant Capacitance Model (CCM) ([5]) that can be used when adsorption equilibria need to be described with an electrostatic model. The parameter *model* in block 1 of the input file must be set to 1. This model requires additional parameters. Two are used to designate the components that have a special meaning in the framework of the CCM (*exponent-nr* and *SOH-nr*). The *inner capacitance* can be estimated based on data obtained from equilibrium experiments (using, e.g., the program *FITEQL* ([8])). It cannot be optimized by *SteadyFit*. The *surface site density* and the *specific surface area* are often available in the literature. The surface component is now XOH rather than XOH_2^+ as used above, since the CCM is usually formulated with the neutral species. The total concentration of the surface component corresponds now to the amount of suspended solid in [g/L]. Since we use another surface component in this example, the equilibrium constants for XOH and XOH_2^+ as well as the rate constant k have different values. Note also that the component SO_4^{2-} has not been included in this calculation.

Listing of gibs3.dat:

Weathering of Gibbsite: Furrer et al, Geochim. Cosmochim. Acta, 53, 595-601 (1988)
rate law $r=k\{\text{XOH}_2^+\}^3$, $k=52.012$; constant capacitance -> new component XOH
=====

```
- (1) calculation type; model; maximum no of iterations; epsilon; output
  1 1 35 1.E-6 3
- (2) model 1 parameters (concentration of solid in g/L with SOH components total concentration)
- exponent-nr; SOH-nr; inner capacitance
  2 1 1.06
```

■ The *exponent-nr* and the *SOH-nr* refer to the number of the components (EXP and XOH) representing the exponential and the surface component SOH. ■

```
- (3) surface site density [mol/g]; specific surface area [m^2/g]
  0.000137 129
- (4) total # of species; total # of components; # of comp. with fixed activity
  8 4 0
- (5) # of immobile species; # of immobile components
  2 2
- (6) # of processes; # of parameters
  2 3
- (7) names of species; Y/-; */-; logK; A-matrix; print
-      Y/-      */-      logK      XOH      EXP      Al3+      H+      print
H+      -      -      0.0      0      0      0      +1      T
OH-      -      -      -14.0      0      0      0      -1      T
Al+3      -      -      0.0      0      0      +1      0      T
Al(OH)+2      -      -      -5.0      0      0      +1      -1      T
Al(OH)2+      -      -      -10.1      0      0      +1      -2      T
Al(OH)3      -      -      -16.0      0      0      +1      -3      T
XOH2+      -      -      7.5      +1      1      0      1      T
XOH      -      -      0.0      +1      0      0      0      T
```

■ Since the constant capacitance model is usually formulated using an SOH component, XOH is used here instead of XOH_2^+ . Note the changes in the constants. ■

```
- (8) names of new components; X/Y/-; L-matrix; logX; T; charge; print
-n\o      Y/X/-      XOH      EXP      Al3+      H+      logX      Total Charge print
XOH      -      +1      0      0      0      -6      8.174      0      T
EXP      -      0      +1      0      0      -6      0      0      T
Al+3      -      0      0      +1      0      -6      0      +3      T
H+      -      0      0      0      +1      -6      0      +1      T
```

■ In the constant capacitance model (*model* = 1) the total concentration of the surface component XOH is the concentration of suspended solid in em g/L. ■

```
- (9) slow processes
- description of processes; names of processes
  inflow_of_solution      inflow
  dissolution_of_Al(OH)3      dissol
- (10) names of species; F-matrix: stoichiometry of species i in process 1
```

```

-          inflow  dissol
H+          +2      0
OH-         0      +3
Al+3        0      +1
Al(OH)+2    0      0
Al(OH)2+    0      0
Al(OH)3     0      0
XOH2+       0      0
XOH         0      0
- (11) RT[l] type of rate equation: 0 order (0), 1st order(1), power law (2)
-          inflow  dissol
          0      2
- (12) names of species; N-matrix power of species i in process 1
-          inflow  dissol
H+          0      0
OH-         0      0
Al+3        0      0
Al(OH)+2    0      0
Al(OH)2+    0      0
Al(OH)3     0      0
XOH2+       0      3
XOH         0      0
- (13) names of parameters (v FIRST); W-matrix power of parameter m in process 1
-          inflow  dissol
v          +1      0
c          +1      0
k          0      +1
- (8) names for parameters; X/-; */-; P: parameter values (units: mol, dm, s)
- FIRST parameter flow velocity v = 1/tau (units equal to a 1st order reaction constant)
v          -      -      3.17E-7
c          -      -      5.00E-05
k          -      -      52.012

```

■ Note that because XOH is used instead of XOH_2^+ , k has a different value now. ■

6.4 Calculations for sensitivity plot (*CalcType* = 4)

In a sensitivity plot, concentration(s) are plotted as a function of system parameter values. This allows the user to see how sensitive the concentration of a certain species (or the total concentration of a component) is with respect to an equilibrium constant or a process parameter. With this information, it can for instance be determined whether from the experimental data available the unknown parameters can be optimised. If the concentration measured is not sensitive with respect to the parameters to be fitted, then the optimisation procedure will hardly give a satisfactory result. All system parameters are varied between a minimal and a maximal value (which are provided by the user as a *factor*, see the comments below).

Listing of gibs4.dat:

Weathering of Gibbsite: Furrer et al. (1989), Geochim. Cosmochim. Acta, 53, 595-601
Rate law: $r=k\{XOH2^+\}$, $k=1.4E-10$

```
=====
- (1) calculation type; model; maximum no of iterations; epsilon; output
  4 0 35 1.E-10 3
- (4) total # of species; total # of components; # of comp. with fixed activity
  12 4 0
- (5) # of immobile species; # of immobile components
  3 1
- (6) # of processes; # of parameters
  2 3
- (7) names of species; Y/-; */-; logK; A-matrix; print
      Y/-      */-      log K   XOH2+   Al3+   SO4-2   H+   print
H+      -      -      0.0      0      0      0      +1   T
OH-      -      -     -14.0     0      0      0      -1   F
SO4-2    -      -      0.0      0      0      +1      0   F
Al+3     -      -      0.0      0      +1      0      0   F
Al(OH)+2 -      -      -5.0      0      +1      0      -1   F
Al(OH)2+ -      -     -10.1     0      +1      0      -2   F
Al(OH)3   -      -     -16.0     0      +1      0      -3   F
Al(OH)4-  -      -     -23.0     0      +1      0      -4   F
AlSO4+    -      -      3.2      0      +1      +1      0   F
XOH2+     -      -      0.0      +1      0      0      0   F
XOH       -      -      -7.5     +1      0      0      -1   F
XS04-     -      -      4.5      +1      0      +1      0   F
- (8) names of new components; Y/-; L-matrix; logX; T; charge; print
-n\o      X/Y/-      XOH2+   Al3+   SO4-2   H+   log X   Total Charge print
XOH2+     -      +1      0      0      0      -6   1E-4   +1   F
Al+3      -      0      +1      0      0      -6      0   +3   F
SO4-2     -      0      0      +1      0      -6      0   -2   F
H+        -      0      0      0      +1      -6      0   +1   F
- (9) slow processes
- description of processes; names of processes
      inflow_of_solution      inflow
      dissolution_of_Al(OH)3    dissol
- (10) names of species; F-matrix: stoichiometry of species i in process 1
      inflow      dissol
H+      +2      0
OH-      0      +3
SO4-2    +1      0
Al+3      0      +1
Al(OH)+2  0      0
Al(OH)2+  0      0
Al(OH)3   0      0
Al(OH)4-  0      0
AlSO4+    0      0
XOH2+     0      0
XOH        0      0
XS04-      0      0
- (11) RT[l] type of rate equation: 0 order (0), 1st order (1), power law (2)
      inflow      dissol
      0          2
- (12) names of species; N-matrix: power of species i in process 1
      inflow      dissol
H+      0      +0.4
```

OH-	0	0
SO4-2	0	0
Al+3	0	0
Al(OH)+2	0	0
Al(OH)2+	0	0
Al(OH)3	0	0
Al(OH)4-	0	0
AlSO4+	0	0
XOH2+	0	0
XOH	0	0
XSO4-	0	0

- (13) names of parameters (v FIRST); W-matrix: power of parameter m in process 1

-	inflow	dissol
v	+1	0
c	+1	0
k	0	+1

- (14) names of parameters; X/-; */-; P: parameter values (units: mol, dm, s)

- FIRST parameter flow velocity v

v	-	-	3.17E-07
c	-	-	5.00E-05
k	-	-	1.4E-10

- (19) # of datapoints

21

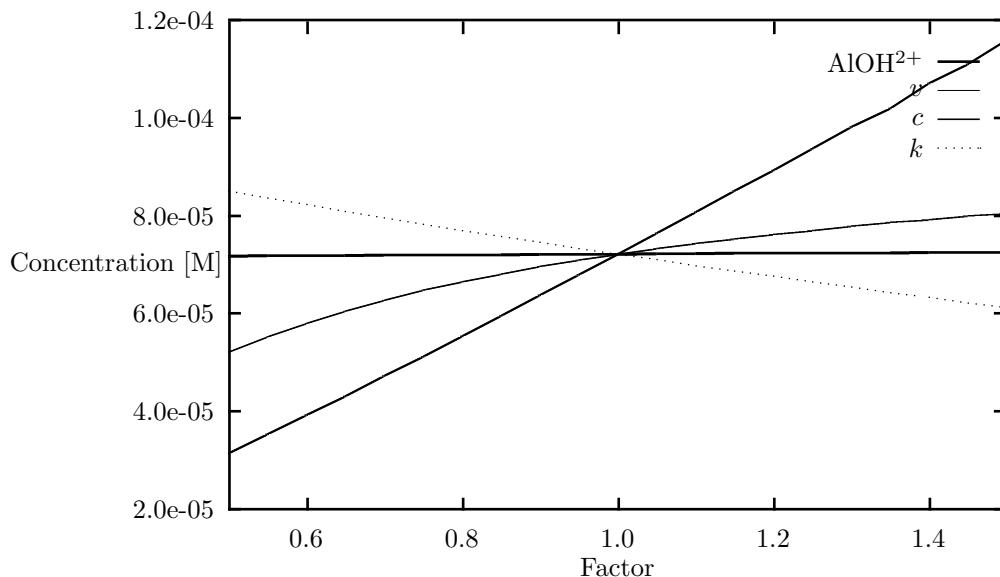
■ For every equilibrium constant $K[i]$ and every parameter $P[m]$, 21 calculations are performed where $K[i]$ and $P[m]$ are set to 21 values between $min.-factor \cdot K[i]$ and $max.-factor \cdot K[i]$ ($P[m]$ respectively) while all other $K[i]$ and $P[m]$ are held at the value specified in the input file. See Figure 2 for the result of this calculation. If the constant capacitance model is used ($model = 1$), the capacitance and the surface site density are included in the serial calculation as well. ■

- (20) min.-factor; max.-factor

0.5	1.5
-----	-----

■ See comment above. ■

Figure 2: Sensitivity plot of the proton concentration as a function of the values of the equilibrium constant for AlOH^{2+} , the flow velocity v , the inflow concentration c and the rate constant k . $[\text{H}^+]$ is most sensitive with respect to k and least sensitive with respect to the equilibrium constant for AlOH^{2+} for the system defined by the input file.



6.5 χ^2 plot in parameter space ($\text{CalcType} = 5$)

Before seeking to optimise kinetic and possibly thermodynamic constants it is often advantageous to know whether there exists a (hopefully global) minimum of the χ^2 function in the n-dimensional space of the constants fitted in the vicinity of the first guess of these constants. With *SteadyFit*, this can easily be accomplished. Three additional parameters need to be specified: *min.-factor*, *max.-factor* and the number of points in that range for each constant investigated. This can easily lead to thousands of *STEADYQL* calculations: if there are, e.g., 30 datapoints and 2 constants investigated, then 30 points per constant results in 54'000 calculations!

Listing of gibs5.dat:

Weathering of Gibbsite: Furrer et al. (1989), *Geochim. Cosmochim. Acta*, 53, 595-601
Rate law: $r=k\{\text{XOH}_2^+\}$; data for Chi2 plot around $k=1.4\text{E}-10$;

```
=====
- (1) calculation type; model; maximum no of iterations; epsilon; output
  5 0 35 1.E-10 33
- (4) total # of species; total # of components; # of comp. with fixed activity
  12 4 0
- (5) # of immobile species; # of immobile components
  3 1
- (6) # of processes; # of parameters
  2 3
- (7) names of species; Y/-; */-; logK; A-matrix; print
-      Y/-      */-      log K      XOH2+      Al3+      S04-2      H+      print
H+      Y      -      0.0      0      0      0      +1      T
OH-      -      -      -14.0      0      0      0      -1      T
S04-2      -      -      0.0      0      0      +1      0      T
Al+3      -      -      0.0      0      +1      0      0      T
Al(OH)+2      -      -      -5.0      0      +1      0      -1      T
Al(OH)2+      -      -      -10.1      0      +1      0      -2      T
```



```

Al(OH)3      -      -      -16.0      0      +1      0      -3      T
Al(OH)4-     -      -      -23.0      0      +1      0      -4      T
AlSO4+       -      -      3.2        0      +1      +1      0      T
XOH2+        -      -      0.0        +1      0      0      0      T
XOH          -      -      -7.5       +1      0      0      -1      T
XS04-        -      -      4.5        +1      0      +1      0      T
- (8) names of new components; Y/-; L-matrix; logX; T; charge; print
-n\o          X/Y/-      XOH2+      Al3+      S04-2      H+      log X      Total Charge print
XOH2+         -          +1          0          0          0          -6      1E-4      +1      T
Al+3          -          0          +1          0          0          -6          0      +3      T
S04-2         -          0          0          +1          0          -6          0      -2      T
H+            -          0          0          0          +1          -6          0      +1      T
- (9) slow processes
- description of processes; names of processes
  inflow_of_solution      inflow
  dissolution_of_Al(OH)3   dissol
- (10) names of species; F-matrix: stoichiometry of species i in process 1
-      inflow      dissol
H+      +2          0
OH-      0          +3
S04-2    +1          0
Al+3      0          +1
Al(OH)+2  0          0
Al(OH)2+  0          0
Al(OH)3   0          0
Al(OH)4-  0          0
AlSO4+    0          0
XOH2+     0          0
XOH        0          0
XS04-      0          0
- (11) RT[l] type of rate equation: 0 order (0), 1st order (1), power law (2)
-      inflow      dissol
      0          2
- (12) names of species; N-matrix: power of species i in process 1
-      inflow      dissol
H+      0          +0.4
OH-      0          0
S04-2    0          0
Al+3      0          0
Al(OH)+2  0          0
Al(OH)2+  0          0
Al(OH)3   0          0
Al(OH)4-  0          0
AlSO4+    0          0
XOH2+     0          0
XOH        0          0
XS04-      0          0
- (13) names of parameters (v FIRST); W-matrix: power of parameter m in process 1
-      inflow      dissol
v      +1          0
c      +1          0
k        0          +1
- (14) names of parameters; X/-; */-; P: parameter values (units: mol, dm, s)
- FIRST parameter flow velocity v
v      X      -      3.17E-07
c      -      -      5.00E-05
k      -      *      1.4E-10
- (17) # of serial datapoints
21
- (18) serial data (id, v, H+, rel(H+), abs(H+))
01      1.58E-07  4.9590E-05  0.05  0.0
02      1.74E-07  5.6299E-05  0.05  0.0
03      1.90E-07  5.5941E-05  0.05  0.0
04      2.06E-07  6.1185E-05  0.05  0.0
05      2.22E-07  6.4755E-05  0.05  0.0
06      2.38E-07  6.3639E-05  0.05  0.0
07      2.54E-07  6.8542E-05  0.05  0.0
08      2.69E-07  6.8316E-05  0.05  0.0
09      2.85E-07  6.8509E-05  0.05  0.0
10      3.01E-07  7.0932E-05  0.05  0.0
11      3.17E-07  7.3696E-05  0.05  0.0

```

```

12      3.33E-07  6.9632E-05  0.05  0.0
13      3.49E-07  7.2298E-05  0.05  0.0
14      3.65E-07  7.7301E-05  0.05  0.0
15      3.80E-07  7.9580E-05  0.05  0.0
16      3.96E-07  8.0190E-05  0.05  0.0
17      4.12E-07  8.0894E-05  0.05  0.0
18      4.28E-07  8.1909E-05  0.05  0.0
19      4.44E-07  7.9026E-05  0.05  0.0
20      4.60E-07  7.9846E-05  0.05  0.0
21      4.75E-07  7.8676E-05  0.05  0.0
- (21) # of datapoints (k)
31

```

■ For every equilibrium constant K and parameter P labelled with an * 31 datapoints are calculated and the Levenberg-Marquardt merit function χ^2 is computed ([4]). This allows the user to check whether there exists a minimum in χ^2 in the vicinity of the initial guess of the parameters to be optimised (see Figure (3). Here, the values of the dependent variable ($[H^+]$) are the same as the ones used in the next sample calculation but the value for k is the true one. ■

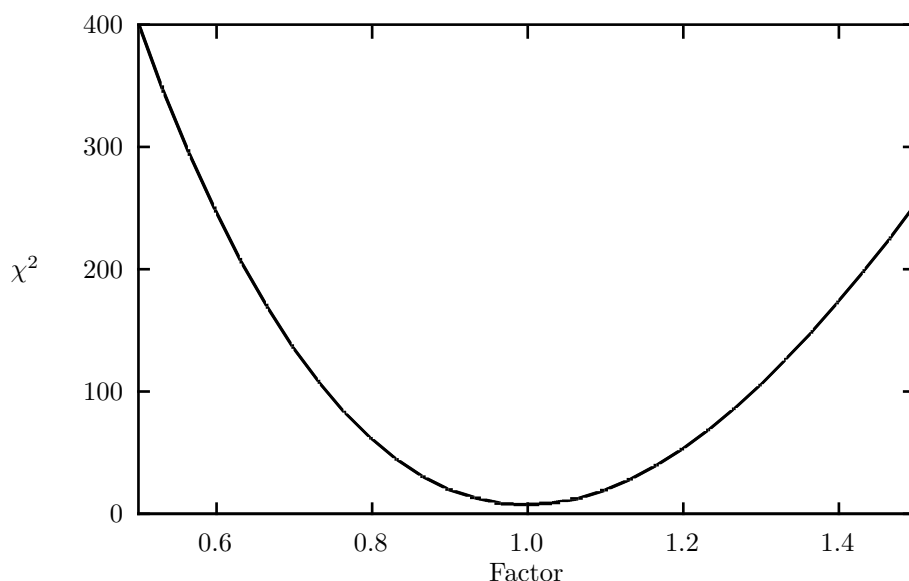
```

- (22) min.-factor; max.-factor
0.5  1.5

```

■ As for $CalcType = 4$, the parameters (with an *) are varied between $min.-factor*parameter$ and $max.-factor*parameter$. ■

Figure 3: The χ^2 merit function as a function of the value of k , expressed as *factor* in the equation $k = \text{factor} \cdot k_{\text{initial}}$.



6.6 SteadyFit: optimisation of constants (*CalcType* = 3)

The final sample calculation demonstrates the actual *SteadyFit*-calculation. It is the optimisation of kinetic and thermodynamic constants on experimental data. Its calculation type is 3.

Listing of gibbs6.dat:

Weathering of Gibbsite: Furrer et al. (1989), Geochim. Cosmochim. Acta, 53, 595-601
Rate law: $r = k\{XOH_2^+\}$; fitting $k (=1.4E-10)$;

```
=====
- (1) calculation type; model; maximum no of iterations; epsilon; output
  3 0 35 1.E-10 33
- (4) total # of species; total # of components; # of comp. with fixed activity
  12 4 0
- (5) # of immobile species; # of immobile components
  3 1
- (6) # of processes; # of parameters
  2 3
- (7) names of species; Y/-; */-; logK; A-matrix; print
-      Y/-      */-      log K  XOH2+  Al3+  SO4-2  H+  print
H+      Y      -      0.0      0      0      0      +1  T
OH-     -      -      -14.0     0      0      0      -1  T
SO4-2   -      -      0.0      0      0      +1      0  T
Al+3    -      -      0.0      0      +1      0      0  T
Al(OH)+2 -      -      -5.0     0      +1      0      -1  T
Al(OH)2+ -      -      -10.1    0      +1      0      -2  T
Al(OH)3  -      -      -16.0    0      +1      0      -3  T
Al(OH)4- -      -      -23.0    0      +1      0      -4  T
AlSO4+   -      -      3.2      0      +1      +1      0  T
XOH2+    -      -      0.0      +1      0      0      0  T
XOH       -      -      -7.5     +1      0      0      -1  T
XS04-    -      -      4.5      +1      0      +1      0  T
```

■ The Y in the column Y/- signifies that serial y-data is provided for the concentration of the species H⁺. If a equilibrium constant is optimised as well, put a * in the appropriate row. ■

```
- (8) names of new components; X/Y/-; L-matrix; logX; T; charge; print
```

-n\o	X/Y/-	XOH2+	Al3+	SO4-2	H+	log X	Total	Charge	print
XOH2+	-	+1	0	0	0	-6	1E-4	+1	T
Al+3	-	0	+1	0	0	-6	0	+3	T
SO4-2	-	0	0	+1	0	-6	0	-2	T
H+	-	0	0	0	+1	-6	0	+1	T

■ If there are x-serial data for a component (e.g. different amounts of suspended solid, i.e. different total XOH_2^+ concentrations, put an X in the column $X/Y/-$ in the appropriate row). If there are y-serial data for a component (e.g. if the total dissolved aluminium has been measured) put a Y in the column $X/Y/-$.
■

```
- (9) slow processes
- description of processes; names of processes
  inflow_of_solution      inflow
  dissolution_of_Al(OH)3  dissol
- (10) names of species; F-matrix: stoichiometry of species i in process 1
-      inflow  dissol
H+      +2      0
OH-      0      +3
SO4-2    +1      0
Al+3      0      +1
Al(OH)+2  0      0
Al(OH)2+  0      0
Al(OH)3    0      0
Al(OH)4-   0      0
AlSO4+     0      0
XOH2+      0      0
XOH        0      0
XS04-      0      0
- (11) RT[l] type of rate equation: 0 order (0), 1st order (1), power law (2)
-      inflow  dissol
      0      2
- (12) names of species; N-matrix: power of species i in process 1
-      inflow  dissol
H+      0      +0.4
OH-      0      0
SO4-2    0      0
Al+3      0      0
Al(OH)+2  0      0
Al(OH)2+  0      0
Al(OH)3    0      0
Al(OH)4-   0      0
AlSO4+     0      0
XOH2+      0      0
XOH        0      0
XS04-      0      0
- (13) names of parameters (v FIRST); W-matrix: power of parameter m in process 1
-      inflow  dissol
v      +1      0
c      +1      0
k      0      +1
- (14) names of parameters; X/-; */-; P: parameter values (units: mol, dm, s)
- FIRST parameter flow velocity v
v      X      -      3.17E-07
c      -      -      5.00E-05
k      -      *      1.E-9
```

■ The X in the column $X/-$ signifies that x-serial data is provided for the parameter v . The $*$ in the column $*/-$ signifies that the parameter k shall be optimised. Provide an initial (intelligent) guess for the parameters you want to optimise. ■

```
- (17) # of serial datapoints (x-values = v)
21
```

■ 21 datapoints (experimental) are provided in the next block. ■

```
- (18) serial data (id, v, H+, rel(H+), abs(H+))
01      1.58E-07      4.9590E-05      0.05      0.0
02      1.74E-07      5.6299E-05      0.05      0.0
03      1.90E-07      5.5941E-05      0.05      0.0
04      2.06E-07      6.1185E-05      0.05      0.0
05      2.22E-07      6.4755E-05      0.05      0.0
```

06	2.38E-07	6.3639E-05	0.05	0.0
07	2.54E-07	6.8542E-05	0.05	0.0
08	2.69E-07	6.8316E-05	0.05	0.0
09	2.85E-07	6.8509E-05	0.05	0.0
10	3.01E-07	7.0932E-05	0.05	0.0
11	3.17E-07	7.3696E-05	0.05	0.0
12	3.33E-07	6.9632E-05	0.05	0.0
13	3.49E-07	7.2298E-05	0.05	0.0
14	3.65E-07	7.7301E-05	0.05	0.0
15	3.80E-07	7.9580E-05	0.05	0.0
16	3.96E-07	8.0190E-05	0.05	0.0
17	4.12E-07	8.0894E-05	0.05	0.0
18	4.28E-07	8.1909E-05	0.05	0.0
19	4.44E-07	7.9026E-05	0.05	0.0
20	4.60E-07	7.9846E-05	0.05	0.0
21	4.75E-07	7.8676E-05	0.05	0.0

■ Every data point has a label of up to 4 characters which goes in the first column of block 18. The serial data must be provided in the sequence corresponding to the X 's and Y 's in the input file. For every y -variable, a relative error (rel), σ_{rel} , and an absolute error (abs), σ_{abs} , must be provided. If there are several x - and y -variables they must be listed in the sequence $x^1, x^2, \dots, y^1, \sigma_{rel}^1, \sigma_{abs}^1, y^2, \sigma_{rel}^2, \sigma_{abs}^2, \dots$ per data point. The y -values used in this example have been calculated with $CalcType = 2$ and then modified by adding a random change of up to 5%, the error is therefore assumed to be 5%. ■

Listing of gibs6.out:

```

Problem title:
Weathering of Gibbsite: Furrer et al. (1989), Geochim. Cosmochim. Acta, 53, 595-601
Rate law: r=k{XOH2+}; fitting k (=1.4E-10);

Input file:
GIBS6.DAT

Input data for verification
=====

Values for logK and parameters correspond to the first guess if
the constants are fitted.

Components:
=====

- mobile : 3
  Al+3, SO4-2, H+
- immobile : 1
  XOH2+

Number of components with fixed activity : 0

Species :
=====

- mobile : 9
  H+, OH-, SO4-2, Al+3, Al(OH)+2, Al(OH)2+, Al(OH)3,
  Al(OH)4-, AlSO4+
- immobile : 3
  XOH2+, XOH, XSO4-

Mass-action equations:
=====

[H+]          = 10^ 0.000 [H+]
[OH-]         = 10^-14.00 [H+]^(-1.)
[SO4-2]       = 10^ 0.000 [SO4-2]
[Al+3]        = 10^ 0.000 [Al+3]
[Al(OH)+2]    = 10^-5.000 [Al+3] [H+]^(-1.)
[Al(OH)2+]    = 10^-10.10 [Al+3] [H+]^(-2.)
[Al(OH)3]     = 10^-16.00 [Al+3] [H+]^(-3.)
[Al(OH)4-]    = 10^-23.00 [Al+3] [H+]^(-4.)

```

```

[AlSO4+]      = 10^ 3.200 [Al+3] [SO4-2]
[XOH2+]       = 10^ 0.000 [XOH2+]
[XOH]         = 10^-7.500 [XOH2+] [H+] ^(-1.)
[XSO4-]       = 10^ 4.500 [XOH2+] [SO4-2]

```

Processes:
=====

Number : 2

```

inflow      : R1  = v c
dissol      : R2  = k [H+] ^ 0.400

```

Parameters:
=====

Number : 3

Values :

```

v      : 3.170E-07
c      : 5.000E-05
k      : 1.000E-09

```

S[l,j] for mobile components
=====

l	id	Al+3	SO4-2	H+	Charge balance
1	inflow	0.	1.	2.	0.0
2	dissol	1.	0.	-3.	0.0

Parameters which are to be fitted:
=====

The following rate constants:
k

Serial data:
=====

x-variable(s):

Nr	id	v
1	01	1.580E-07
2	02	1.740E-07
3	03	1.900E-07
4	04	2.060E-07
5	05	2.220E-07
6	06	2.380E-07
7	07	2.540E-07
8	08	2.690E-07
9	09	2.850E-07
10	10	3.010E-07
11	11	3.170E-07
12	12	3.330E-07
13	13	3.490E-07
14	14	3.650E-07
15	15	3.800E-07
16	16	3.960E-07
17	17	4.120E-07
18	18	4.280E-07
19	19	4.440E-07
20	20	4.600E-07
21	21	4.750E-07

y-variable(s):

Nr	id	H+	sigma
1	01	4.959E-05	2.479E-06
2	02	5.630E-05	2.815E-06

3	03	5.594E-05	2.797E-06
4	04	6.118E-05	3.059E-06
5	05	6.475E-05	3.238E-06
6	06	6.364E-05	3.182E-06
7	07	6.854E-05	3.427E-06
8	08	6.832E-05	3.416E-06
9	09	6.851E-05	3.425E-06
10	10	7.093E-05	3.547E-06
11	11	7.370E-05	3.685E-06
12	12	6.963E-05	3.482E-06
13	13	7.230E-05	3.615E-06
14	14	7.730E-05	3.865E-06
15	15	7.958E-05	3.979E-06
16	16	8.019E-05	4.009E-06
17	17	8.089E-05	4.045E-06
18	18	8.191E-05	4.095E-06
19	19	7.903E-05	3.951E-06
20	20	7.985E-05	3.992E-06
21	21	7.868E-05	3.934E-06

=====

R E S U L T S

=====

The Levenberg-Marquardt procedure converged after 4 cycles.

The last Chi^2 value is: 7.297E+00

There are nu = 20 degrees of freedom.

Goodness of fit:

$Q(\nu/2, \text{Chi}^2/2) = 9.956\text{E-}01$

--> Q is the probability that the given Chi^2 value is exceeded by chance!

The final values for the constants fitted are:

Rate constants:

k : 1.399E-10

7 Glossary

A matrix: The **A** matrix contains the stoichiometric coefficients of the component k (columns) in the species' i (rows) formation reactions (fast processes).

Components: From the list of species we have to select a set of components which are a complete and independent set of reactants that allow the representation of all species as the product of a reaction involving only components. No component can be represented as a product of a reaction involving only the other components. We distinguish between components with known total concentration, components with fixed free concentration and components for which neither is known. For immobile components the total concentration must be known and therefore belongs to the definition of the system.

Database: To define the STEADYQL database the following steps are needed:

- Identify the species
- Select a set of components from the species and formulate the equilibrium reactions that lead to the formation of the species using only components.
- Identify the slow processes.
- Assign a rate equation to every process.
- Write the input file where the so-obtained definition of the system is described in terms of the **A**, **F**, **N**, **W**, and **L** matrices and the **K**, **T**, **X** and **P** vectors. For calculation types 3 (fitting) and 5 (χ^2 plot) experimental data belong to the definition of the database.

Dependent Variables: The values of the dependent variable(s) are the result of an experiment and can be one or more species' concentration or components' total concentration. Associated with every value of the dependent variable is a relative and an absolute error, specified by the user.

Error: see **Dependent Variables**

Flow Velocity: The flow velocity v can be obtained using the relation $v = \tau^{-1}$, where τ is the residence time. If the fluxes are given as fluxes through a volume, then their units are $\text{mol dm}^{-3} \text{s}^{-1}$ and the corresponding flow velocity has the units of a first order rate constant, s^{-1} . If the fluxes are given as fluxes through an area (for instance to describe annual precipitation) then their units are $\text{mol dm}^{-2} \text{s}^{-1}$ and the corresponding flow velocity has units of dm s^{-1} .

F matrix: The **F** matrix contains the stoichiometric coefficients of species i (rows) in the slow process l (columns).

Immobile Species/Components: Immobile species and components are e.g. products of adsorption reactions and cannot leave the system. They are defined as opposite to mobile components and species.

Independent Variables: The independent variable(s) can be controlled by the experimenter. They correspond to the flow velocity and the concentration of the inflow solutions.

Input file format: The input file format is explained in the section "Input file format". The input file can be edited using any ASCII-editor.

logK vector: The **logK** vector contains the logarithmic value of the equilibrium constants for the formation of all species.

logX vector: The **logX** vector contains the log value of the free concentration of all components. In the input file either specify the first guess or, if the free concentration of a component is fixed, the actual free concentration.

L matrix: The **L** matrix can be used to transform the old set of components (columns) to a new set of components (rows) without having to rewrite the whole input file. If no transformation is made, then just specify the **L** matrix as a unity matrix in the input file.

Mobile Species/Components: Mobile species and components are in solution and leave the system through outflow.

N matrix: The **N** matrix contains the exponents of species i (rows) in the rate equation belonging to the slow process l (columns).

Normalised sensitivity coefficient: see **Sensitivity Analysis**

output parameter: The parameter *output* is the sum of any of the following numbers (not all are applicable for all calculation types):

Number	Specification of output
1	print input data for verification and headers
2	print sensitivities
4	print covariance and curvature matrix
8	print residuals
16	print sensitivities only (<i>CalcType</i> = 2)
32	serial concentrations on 1 line

Processes: The advantage of the *STEADYQL* formalism is that it does not lock the system into a particular time frame. Rather, it distinguishes between three distinct time frames (fast, slow, very slow), relative to the residence time of the mobile species in the system:

1. fast processes can be described using equilibrium thermodynamics;
2. slow processes can be described by kinetic equations;
3. very slow processes are not considered explicitly (i.e. components taking part in a very slow reaction have a constant concentration or a very small rate constant).

Process Parameters: Process parameters are the flow velocity, the concentration of the solutions in the inflow and all rate constants. They appear all in the rate equations describing the slow processes.

P vector: The **P** vector contains the values for the process-parameters. Note that the flow velocity v has to be the first parameter in the list.

Rate Equations: For every slow process a rate equation has to be included in the data base. Note that a rate law of the form

$$R = k_1[\text{H}^+] + k_2[\text{H}^+]^2$$

describes in fact two separate processes: one of first order in $[\text{H}^+]$ and the other one of second order in $[\text{H}^+]$.

S matrix: The **S** matrix lists the stoichiometric coefficients of component k in process m . It is calculated by *SteadyFit* and printed to the output file.

Sensitivity Analysis: After a steady-state calculation, a sensitivity analysis is performed. The sensitivity analysis calculates the sensitivity of the species' concentration to changes in the system parameters. The sensitivity is expressed in terms of the normalised sensitivity coefficient, $Q_{i,m}$, which is defined by

$$Q_{i,m} = \frac{\partial \ln C_i}{\partial \ln P_m} = \frac{\partial C_i}{\partial P_m} \frac{P_m}{C_i} \approx \frac{\Delta C_i}{\Delta P_m} \frac{P_m}{C_i}$$

where C_i is the concentration of species i and P_m is the values of parameter m for process parameters. The normalised sensitivity coefficient for equilibrium constants is calculated analogously. For practical purposes, the sensitivity coefficients can be interpreted in the following way: a one percent change in the value of the parameter m will cause a $Q_{i,m}$ change in the concentration of species i .

Sequence of species/components in the input file: The sequence of components and species in the various matrices is fixed due to the mathematical formulation of the problem. For species, first list the mobile and then the immobile compounds. For components, the sequence is immobile then mobile components and finally components with fixed activity.

Species: The species are the chemical compounds that occur in the system in significant concentration.

System Parameters: The system parameters include all process-parameters and all equilibrium constants. In *SteadyFit*, one or more of the system parameters can be fitted to a set of experimental data.

T vector: The **T** vector contains the total concentration for any component, which has to be specified by the user for immobile components and is calculated by the program for all others.

Units:	Concentration:	$mol\ dm^{-3}$	
	Flow velocity:	s^{-1}	or $dm\ s^{-1}$
	Fluxes:	$mol\ dm^{-3}\ s^{-1}$	or $mol\ dm^{-2}\ s^{-1}$

Equilibrium constants and rate constants have the usual units.

W matrix: The **W** matrix contains the exponent of the process parameter m (rows) in the slow process l (columns).

8 Changes

new version	change
6.2 (24.7.95)	<p>A label of up to 4 characters must now be attached to every data point in the serial data block (block 18). This label must be given in the first column.</p> <p>The error associated with serial Y-data must now be specified as a relative error σ_{rel} (e.g. 0.05 for 5 %) and an absolute error σ_{abs} (which may be zero). The error σ is then computed according to $\sigma = \sigma_{rel}y + \sigma_{abs}$. The serial data specified in the serial data block (block 18) now takes the form $id, x^1, x^2, \dots, y^1, \sigma_{rel}^1, \sigma_{abs}^1, y^2, \sigma_{rel}^2, \sigma_{abs}^2, \dots$ where the index refers to the first, second, ... x and y variable, respectively (not to the first, second, ... data point).</p>

9 Bugs

Unfortunately, no program and no manual are free of bugs. If you find some, please send an e-mail to gfeller@ito.umnw.ethz.ch. Also, if you find parts or all of this manual unreadable, feel free to give me hints on how to improve things.

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