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# CHESS Tutorial and Cookbook

Updated for version 2.4

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CHESS stands for CHEmical Equilibrium Speciation with Surfaces  
Actual version: 2.4.

CHESS is on the internet: <http://chess.ensmp.fr>  
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# 1 Introduction

Geochemical models are used to shed light on important issues such as the solubility of contaminants, their reactivity with respect to a soil or rock matrix and their complexation reactions with other chemical species. They are specialized calculation tools which solve non-linear multi-dimensional sets of equations to calculate the equilibrium state or a kinetic path of complex geochemical systems. They also read, process and understand extended databases which contain thermodynamic properties of the species. CHESS, which stands for **C**HeMical **E**quilibrium with **S**pecies and **S**urfaces, is such a computer model and deals with a large number of processes and features, such as:

- **thermodynamic equilibrium with mineral, gaseous or colloidal phases**

A complete species-spectra is calculated where equilibrium of one or more phases can be imposed. For example, one sometimes needs to impose a partial CO<sub>2</sub> pressure, or to calculate the amount of calcium ions into a solution in equilibrium with calcite.

- **oxidation and reduction**

When the redox-potential is given, the model calculates the equilibrium state of the solution with respect to the correct oxidation state. Redox may be triggered in different ways, e.g. by imposing oxygen or by providing the Eh or pe of the solution. In case of redox disequilibrium, it is possible to decouple specific species from the redox reactions.

- **precipitation and dissolution of mineral phases**

When a mineral phases appears to be oversaturated, then CHESS precipitates the mineral and recalculates the equilibrium state. On the other hand, dissolution will occur when the mineral is undersaturated. This process is repeated until none of the phases is under- or oversaturated. This feature can be turned off (or fine-tuned) by the user.

- **formation and dissolution of colloidal phases**

Colloids may be formed if they appear to be oversaturated with respect to the aqueous composition. When undersaturated, colloids will dissolve. This feature can be turned on or off by the user.

- **surface complexation**

Calculation of interaction between aqueous species and reactive surface groups of mineral or colloidal species present in solution is based on the surface complexation theory with electrostatic correction. The latter uses the double layer theory.

- **cation exchange**

Cation exchange with minerals or colloids is possible instead of (or together with) surface complexation. For example, clay particles may contain cation exchange and surface complexation sites and CHESS will calculate the equilibrium state taking into account both site-types.

- **multi-site reactions**

A colloidal or mineral surface (of inorganic or organic nature) may contain more than one site. More precisely, the number of sites per surface is unlimited. Hence the *continuous site distribution model* can be emulated using a large enough number of sites. You could try hundred sites, for example!

- **multi-surface reactions**

The number of reactive mineral- or colloid surfaces in the system is unlimited, hence enabling the calculation of complex, reactive geochemical systems.

- **reaction paths**

Reaction paths may be provided enabling the solution to evolve from one state to another. Powerful processes such as titration, flushing or mixing of two solutions are available and easy to use.

- **temperature dependence (0 to 300 °C)**

The solution temperature can be set to any value above 0 °C. The database contains polynomial values up to 300 °C for most species.

- **kinetic control of dissolution and precipitation**

Kinetic control of dissolution and precipitation of mineral and colloidal phases can be enabled for any period of time through a general kinetics law including reactive surface area, catalyzing or inhibiting effects and temperature dependence.

In brief, the model fulfills the general modelling-*desiderata* but is clearly evolving to more specifically (colloidal) surface interface processes and heterogeneous reactive systems. This is reflected also in the database which includes colloidal species and reactive sites with a structured but flexible format.

CHESS is written in C++ and is entirely object-oriented, which improves the readability, maintenance and development of the code. CHESS has been developed for coupling purposes with hydrodynamic models. In view of this goal, all basic functions related to database reading and treatment as well as the Newton-Raphson solver are grouped together in a library, CHESSLIB. This library can be linked to any hydrodynamic model and provides access to equilibrium concentrations, sorbed or precipitated quantities and other useful information.

The present tutorial has been conceived to progressively introduce the reader to the *language* and commands of CHESS, making use of practical examples related to laboratory experiences or geochemical systems. This is made easier by the fact that CHESS is based on intuitive keywords and only needs a minimal input from the user. However, chemical models still remain specialist softwares asking for at least a basic knowledge of thermodynamic concepts, surface reactions and modelling formalisms. The more fundamental and theoretical aspects are the subject of a complementary document (van der Lee 1998).

## 2 Getting Started

### 2.1 The keyword concept

CHESS is easy to use, yet it is designed to meet demands of the most complex geochemical modelling needs. This is why CHESS is *keyword* based. In order to communicate with the model, it is necessary to learn some of CHESS' vocabulary, i.e. typical words such as **activity**, **balance**, **bring**, etc. Using a keyword-based approach offers, among others, two main advantages: first, the vocabulary is intuitive, hence easy to remember. Second, the approach is evolutive. Indeed, subsequent options can be conveniently added without invalidating older input scripts.

Executing CHESS without command-line arguments opens CHESS' interactive mode. This mode is an *on-line help* shell allowing the user to interact or communicate with the model. CHESS knows a large number of keywords —many are only needed for complex applications— and it is possible to learn about their usage with the on-line help. For example, typing

```
show keywords
```

in CHESS' interactive mode provides the entire vocabulary of CHESS. More information about a specific keyword is obtained by the command **help**<keyword>, where <keyword> can be any word of CHESS' vocabulary. The following example shows the on-line help feature for keywords **help** and **bring**:

```

                                ---
You're running CHESS: CHemical Equilibrium of Species and Surfaces
    unix version 2.4, patchlevel 1, compiled Wed Dec 9 1998,
                        (c) Jan van der Lee CIG/ENSMP
                                +-
Chess> help help
    gives some basis help, hints and tips. Examples:
        "help"          (general help, shows the commands known by CHESS)
        "help bring"    (shows help on keyword 'bring')
        "help tot"      (shows help on keyword 'total-concentration')
Chess>
Chess> help bring
    sets a reaction path as a function of some variable. Examples:
        "bring pH to 12"
        "bring colloid >Quartz to 10 g/l"
        "bring tot Zn[2+] to 1 mmol/l"
        "bring temperature to 150 C"
        "bring Eh to 700 mV"
Chess> quit
```

The command **quit** terminates the CHESS shell. A complete glossary of keywords is provided for in Appendix C of this manual. An hypertext-based glossary is available on

the CHESS home page<sup>1</sup>

## 2.2 Running your first script!

Any programmer has started with one and the same programme, writing 'hello world' to the screen. Here we would like to introduce a similar custom. Any geochemical modeler should start with the following one-liner: dissolution of quartz in pure water. Quartz will partly solve, releasing  $\text{SiO}_2(\text{aq})$  and protons to the solution. Consequently, the pH is expected vary, but how much exactly? CHESS may tell you this.

We put 10 mg/l of quartz into pure water, and calculate the equilibrium state. We edit an input script which contains only one line. We named it as **myscript.chs** for instance. The script looks like this:

```
mineral Quartz = 10 mg/l
```

We only need to set the total concentration of mineral quartz to the desired concentration, 10 mg/l. Quite simple ! We used the keyword **mineral** in order to explain to the model that quartz is a mineral. Note that CHESS recognizes most units (see appendix A). We run CHESS by typing

```
chess
chess myscript.chs
```

after the prompt. CHESS reads the input script file and subsequently calculates the equilibrium state of the system. The final results, i.e. the species concentrations, saturation indices, solid concentrations etc. are written to an output file named **CHESS.out** by default. This file, which is ASCII text, can be viewed with any editor (emacs, vi, xedit, notepad, etc.) or sent to a printer. More about what the input script and output file may contain will be progressively introduced in this manual. For now, let us just have a quick glance at a part of the output file:

```
[snip]
calculating initial equilibrium...
...the system converged in 6 iterations
...success!

Final equilibrium of the main solution:
=====

State variables and solution characteristics
-----

pH                : 6.83594
ionic strength    : 1.45967e-07
temperature       : 25 Celsius
electrical balance : 1e-25 mol/l
```

---

<sup>1</sup><http://chess.enscm.fr>



water volume : 1 liter

#### Concentrations and activities of relevant species

name:	-----concentration-----		activity (mol/l)	act.coef.
	(mol/l)	(g/l)		
SiO2(aq)	0.00010016	0.0060181	0.00010016	1
H[+]	1.4597e-07	1.4712e-07	1.459e-07	0.99955
HSiO3[-]	7.6619e-08	5.9067e-06	7.6584e-08	0.99955
OH[-]	6.9348e-08	1.1794e-06	6.9317e-08	0.99955
H2SiO4[2-]	5.1684e-14	4.8634e-12	5.1592e-14	0.99821
H6(H2SiO4)4[2-]	1.0851e-16	4.1498e-14	1.0831e-16	0.99821
H4(H2SiO4)4[4-]	2.5684e-25	9.771e-23	2.5501e-25	0.99288

#### Elemental concentrations (mol/l):

species	aqueous	mineral	colloidal	organic	fixed	gaseous	total
H[+]	1.46e-07	0	0	0	0	0	1.46e-07
SiO2(aq)	0.0001002	6.619e-05	0	0	0	0	0.0001664

#### Elemental concentrations (g/l):

species	aqueous	mineral	colloidal	organic	fixed	gaseous	total
H[+]	1.471e-07	0	0	0	0	0	1.471e-07
SiO2(aq)	0.006023	0.003977	0	0	0	0	0.01

#### Gases:

name	fugacity
H2O(g)	0.02598

#### Solids and some characteristic properties:

type:	name:	---concentration-----	---spec. surface---
		(mol/l) (g/l)	(m2/g) (m2/l)
mineral	Quartz	6.619e-05 0.003977	0.01133 4.505e-05

#### Saturation indices of minerals and colloids:

	SI:
colloid >Quartz	0
mineral Ice	-0.1387
mineral Tridymite	-0.1715
mineral Chalcedony	-0.2712
mineral Cristobalite(alpha)	-0.5505
mineral Coesite	-0.81
mineral Cristobalite(beta)	-0.994
colloid >SiO2_am	-1.286
mineral SiO2(am)	-1.286
[snip]	

Interestingly, putting just one mineral in pure water leads to a system of 7 aqueous species and a dozen of potential minerals and colloids!

Note that the interactive mode can be occasionally used for making simple input scripts. For example, we might prefer to create the previous script in interactive mode, and then to save it under the name **myscript.chs**. Here is an example:

```

          ---
You're running CHESS: CHemical Equilibrium of Species and Surfaces
      unix version 2.4, patchlevel 1, compiled Wed Dec 9 1998,
          (c) Jan van der Lee CIG/ENSMP
          +-
Chess> mineral Quartz = 10 mg/l
Chess> save myscript.chs
- saving script file in myscript.chs...OK
Chess>

```

We save the script with keyword **save** followed by the filename. The file **myscript.chs** of our Quartz dissolution example now contains the script:

```

# Input script of CHESS, version 2.4, patch level 1
# Saved on Mon Jan  4 15:36:57 1999
mineral Quartz = 10 mg/l

```

which can be used for future runs. Remark the first two lines, which are *commented out* by a special character, “#”. Each line which has “#” as its first character is disregarded, which allows to add comments to the file. Similarly, each blank line is disregarded also.

This example is, of course, simple enough to be solved without a sophisticated geochemical system solver, such as CHESS. However, it nicely illustrates how elementary problems do not require many lines of error-prone input script. Instead, the input script is as simple as the system “to-be-solved”. The next chapter dwells further on CHESS applications, but we will progressively increase the complexity level.

## 3 Carrying on

Having learned to walk, let's try a jog! In the context of some simple but practical examples, we will introduce new, useful keywords to teach you how to solve for the equilibrium states of aqueous laboratory or natural systems. This chapter deals with the concept of basis species and element speciation, the precipitation and dissolution of colloidal and mineral solids and the redox disequilibrium state. A certain number of new keywords will be introduced in this chapter. A complete glossary of all available units and keywords are respectively given in Appendix A and Appendix C of this manual.

### 3.1 The "basis species" concept

CHESS is, as most modern geochemical models, based on the concept of *basis species*, brought forward by Gibbs in the beginning of this century and mathematically elucidated in the early eighties by Morel (1983). A basic knowledge of this theory, also called the theory of principle components, is required in order to understand input quantities such as total concentrations.

Let us consider the following example. A laboratory experiment consists of studying the thermodynamic equilibrium state of a solution composed of 0.1 mol/l of NaCl and 1 mmol/l of FeCl<sub>3</sub>. The pH is adjusted to a value of 8 by adding sufficient amounts of NaOH. Yet how do we put this chemistry into the model? We know the total amount of elements Cl and Fe, and we have a pH. But nothing can be said about the actual concentration of species Fe(OH)<sup>2+</sup>, for example, and there is an uncertainty about the exact total amount of element Na. One way to proceed is simply to introduce the *total concentration* in element Na, Cl and Fe calculated from the known concentrations of NaCl and FeCl<sub>3</sub> salts. For simplicity, we exclude any colloids precipitation from the system. Here is the input script:

```
pH = 8
tot Na[+] = 0.1 mol/l
tot Fe[3+] = 1 mmol/l
tot Cl[-] = 0.103 mol/l
balance on Na[+]
```

```
exclude colloids
```

Note that Na<sup>+</sup> is written as Na[+] in CHESS language. The use of keyword **tot** (an abbreviation of keyword **total-concentration**) sets the total concentrations of elements Na, Cl and Fe in the system. The command **pH = 8** is of entirely different nature, because it specifies the activity of *species* H<sup>+</sup> and not the concentration of element H. Similarly, we could have written the script as follows:

```
act H[+] = 1e-8
tot Na[+] = 0.1 mol/l
tot Fe[3+] = 1 mmol/l
tot Cl[-] = 0.103 mol/l
```

balance on Na[+]

exclude colloids

which even better stresses the differences between specifying the total concentration of an element versus the concentration (or activity) of a specific species. The keyword **activity** (**act** in short) is used to set the activity of any species. The remaining uncertainty about the total Na concentration is removed by the keyword **balance** which adapts the total Na concentration in order to fulfill the condition of solution electroneutrality.

The results are written in the output file **CHESS.out** by default (see the keyword **output-filename** to modify its name). Here is a first snippet of the file:

```
[snip]
calculating initial equilibrium...
...the system converged in 47 iterations
precipitating Hematite...
    (saturation index: 17.8604)
...the system converged in 1 iterations
...success!
[snip]
```

About 47 Newton-Raphson iterations are needed to equilibrate the system. The system is over-saturated with respect to hematite, and the model decides to precipitate this mineral. Then, convergence is reached immediately. A second snippet of the file reports the concentration and activity of the whole of the aqueous species.

```
[snip]
Concentrations and activities of relevant species
-----
name:                -----concentration-----  activity    act.coef.
                        (mol/l)      (g/l)      (mol/l)
Na[+]                0.10197      2.3443      0.079621    0.78083
Cl[-]                0.10197      3.6149      0.079616    0.78083
NaCl(aq)             0.0010347    0.060473    0.0010593    1.0238
OH[-]                1.2952e-06    2.2029e-05    1.0113e-06    0.78083
NaOH(aq)             1.2475e-08    4.9895e-07    1.2771e-08    1.0238
H[+]                 1.2807e-08    1.2908e-08    1e-08         0.78083
HCl(aq)              1.6627e-10    6.0621e-09    1.7022e-10    1.0238
Fe(OH)3(aq)          1.1069e-12    1.1829e-10    1.1332e-12    1.0238
Fe(OH)4[-]           3.6454e-14    4.5158e-12    2.8464e-14    0.78083
Fe(OH)2[+]           3.1028e-14    2.7882e-12    2.4227e-14    0.78083
FeOH[2+]             1.9683e-18    1.434e-16     7.3164e-19    0.37174
Fe[3+]               1.0504e-23    5.8661e-22    1.1332e-24    0.1079
FeCl2[+]             1.241e-24     1.5729e-22    9.6896e-25    0.78083
```

Elemental concentrations (mol/l):

```
-----
species  aqueous  mineral  colloidal  organic  fixed  gaseous  total
H[+]     1.297e-08  0        0          0        0      0        1.297e-08
Na[+]    0.103     0        0          0        0      0        0.103
```

Fe[3+]	1.174e-12	0.001	0	0	0	0	0.001
Cl[-]	0.103	0	0	0	0	0	0.103

[snip]

The solution has reached electroneutrality, and the final total Na concentration, given in the second table is about 0.103 mol/l. The speciation of chlorine and sodium is quite simple, whereas the iron chemistry is more complex. The proton activity yields precisely  $10^{-8}$ . The activities of the aqueous species are computed with the *truncated Davies* formula. However, it is possible to specify three other alternatives: the *Davies* formula, and two formulae derived from the *Debye-Hückel* theory. These options are discussed in van der Lee (1998).

Taking into account iron speciation, we do not select the most abundant species in our input script. The choice of  $\text{Fe}^{3+}$  was guided by a direct translation of the stoichiometry of the  $\text{FeCl}_3$  salt rather than geochemical insights. Also from a numerical point of view, it was not the most appropriate choice because it leads to a bad trial of the solution. Indeed, at the end of the equilibrium calculation, iron is found in the form of mainly Hematite. So, how to solve for this problem with on the one hand a recipe and on the other hand the model requirements?

The solution is simple, but requires recalculation of the actual total concentrations. It consists of expressing the recipe in terms of initial basis species. Very helpful is to use a *mini-tableau*, as outlined in CHESS' technical report (van der Lee (1998)). Here, we reproduce a mini-tableau for our example, in which we use Hematite as the replacement for  $\text{Fe}^{3+}$  (see Table 3.1).

The concentrations of our new basis are calculated by multiplying the stoichiometric coefficients with the total concentrations corresponding to the recipe of that row and summing up all rows of the column. Note that the total concentration of  $\text{H}^+$  is undefined:  $\text{H}^+$  is constrained by its activity (hence its total concentration *floats*). The species  $\text{H}_2\text{O}$  forms automatically part of the basis and does not need to be included in the basis. Accordingly, the new basis is defined by the following script:

```
pH = 8
tot Na[+] = 0.1 mol/l
tot Hematite = 0.5 mmol/l
tot Cl[-] = 0.103 mol/l
balance on Na[+]
```

```
exclude colloids
```

Running CHESS with this script leads to virtually identical results as the former script, but shows a different numerical behaviour. Here is a snippet of the file **CHESS.out**:

```
[snip]
calculating initial equilibrium...
...the system converged in 10 iterations
...success!
[snip]
```

Hence simply by changing the set of basis species, the model takes only about one fifth of the number of iterations to converge to the same results. The choice of the basis

	Na <sup>+</sup>	Cl <sup>-</sup>	Hematite	H <sup>+</sup>	H <sub>2</sub> O	
Na <sup>+</sup>	1	1	0	0	0	0.1 mol/l
Cl <sup>-</sup>	0	1	0	0	0	0.103 mol/l
Fe <sup>3+</sup>	3	0	0.5	-3	-1.5	0.001 mol/l
H <sup>+</sup>	0	0	0	1	0	?
H <sub>2</sub> O	0	0	0	0	1	55.6 mol/l
Total concentration	0.103	0.1	0.0005	?	55.6 mol/l	

**Table 3.1:** Mini-tableau for a basis swap.

component is of no consequences in our simple example, but it may become much more important for systems including several mineral phases (especially aluminosilicates) or redox species. This behaviour, which is common for all geochemical models (we think), stresses the usefulness of some basic knowledge of not only chemistry, but also of basic concepts in geochemical modelling.

## 3.2 Precipitation and dissolution

The previous example already illustrated how the model accounts for precipitation. Dissolution and precipitation of solid phases (i.e. colloids and minerals) are important geochemical processes, omnipresent in nature. CHESS behaves fairly self-containedly with respect to precipitation and dissolution, in the sense that solid phases are automatically precipitated or dissolved if saturation or undersaturation is reached. In other words, the model assumes thermodynamic equilibrium for all species, including solids such as colloids and minerals.

However, precipitation and dissolution are time-dependent, kinetic processes. Moreover, other, non-thermodynamic processes such as nucleation (for precipitation) or surface availability (for precipitation *and* dissolution) are of fundamental importance to the actual equilibrium concentration of the solids (see e.g. van der Lee (1997) for a section on this matter). In order to anticipate these phenomena, precipitation and dissolution can be disabled or "fine-tuned" for specific case studies, where thermodynamic equilibrium with some minerals is unlikely to be obtained. The most simple tuning options are disabling or enabling dissolution and/or precipitation. More refined adjustment can be obtained by e.g. disabling precipitation or dissolution of specific species only, modifying thermodynamic equilibrium constants, excluding solids from the system, or accounting for kinetic rate laws.

In order to illustrate the precipitation and dissolution options of CHESS, let us consider another experimental system in which we introduce hydrous ferric oxide (HFO in short) colloids at a concentration of 10 mg/l in an electrolyte (NaClO<sub>4</sub>) to initiate a batch sorption experiment. Here is the recipe in CHESS format:

```
pH = 5
tot Na[+] = 0.01 mol/l
tot ClO4[-] = 0.01 mol/l
```

```
balance on ClO4[-]
```

```
colloid >HFO = 10 mg/l
```

Although HFO may be perfectly stable in the experimental conditions, it is thermodynamically less stable than e.g. hematite. And indeed, when running this script CHESS predicts total dissolution of the colloids to form a more stable mineral phase:

```
[snip]
calculating initial equilibrium...
...the system converged in 10 iterations
precipitating Hematite...
  (saturation index: 4.1668)
...the system converged in 1 iterations
...success!
[snip]
```

At this stage, you might want to exclude hematite from the system, using `exclude Hematite`. However, the *mineral* goethite will precipitate instead, hence you still transform HFO in some new phase. You may, however, simultaneously exclude different species, and adding the line `exclude Hematite, Goethite` to the input script leads to stable HFO colloids. But what if we want to add HFO colloids in a system which contains hematite as well? The answer is: modify the precipitation and dissolution behaviour of the system.

The first option is to disable dissolution of HFO, hence disabling precipitation of secondary phases composed of HFO-forming species (principally Fe(III)). Here is the input script for such a system:

```
pH = 5
tot Na[+] = 0.01 mol/l
tot ClO4[-] = 0.01 mol/l
balance on ClO4[-]

colloid >HFO = 10 mg/l
dissolution = disabled of >HFO
```

However, this leads to system deprived of Fe(III) species, which is unlikely to be the case for the real system. Indeed, HFO colloids might look stable but a small fraction will dissolve. In some systems, such as colloidal silica, the dissolved components can play an important role in the reactivity of some species (e.g. uranium, americium) by acting as complexing agents.

Another option is to let the colloids partially dissolve, but to prevent precipitation of new phases. Indeed, precipitation is kinetically controlled and often requires a super-saturated solution to trigger the precipitation process. Hence the following line input could be used instead, where we disable precipitation of hematite phases:

```
precipitation = disabled of Hematite, Goethite
```

or by disabling the entire process of precipitation:

```
precipitation = disabled
```

Disabling precipitation of specific species is different from excluding these species: the keyword `disable precipitation of` only skips the test on the saturation state of the mineral, while the keyword `exclude` leaves a species out of the system. Accordingly, the latter approach enables to examine saturation states by means of the saturation indices.

**Note:** Although colloidal and mineral HFO have identical formation constants, colloidal species will precipitate first. This is a purely arbitrary choice of the model (or, more precisely, of the model-designer), who expects that colloidal phases are formed prior to minerals. One may dislike this choice and alter this behaviour by slightly changing the formation constants of one of the solids, using the `logK` keyword.

### 3.3 Redox disequilibrium

The assumption of thermodynamic equilibrium between all the *redox species* of a geochemical system is not always justified in natural waters, specially at low temperature or low micro-biological activities. In addition, an Eh measure may reflect the predominant redox couple, or at least the fastest to react during the measurement, but not be representative for other redox couples.

The CHESS' command `redox = disabled of` can be used to prevent some specific species representing different oxidation states of an element to be link by equilibrium reactions. Once a redox coupled has been disabled, CHESS considers the disabled species as equivalent to a basis species. The disabled species has thus its own mass balance and independent entry in the input script. The coupled redox species are listed in B.

Let us carry on with a practical example. Groundwaters circulating in a crystalline fractured rock have been sampled in boreholes with a packer design which preserves anoxic conditions. The fractures are filled with carbonates (calcite, siderite), pyrite, quartz and clay minerals. Here is the (simplified) input script for one of the water samples:

```
temp = 12 C
pH = 8.2
Eh = 0.05 V

tot Na[+] = 1500 mg/l
tot Ca[2+] = 24 mg/l
tot Fe[2+] = 0.6 mg/l
tot N2(aq) = 0.1 mg/l
tot SiO2(aq) = 6 mg/l
tot HCO3[-] = 310 mg/l
tot Cl[-] = 2200 mg/l
tot SO4[2-] = 20 mg/l
tot NO3[-] = 9 mg/l

redox = disabled of NO3[-]
precipitation = disabled
```



Quartz	0.27
Calcite	0.10
Fe(OH) <sub>3</sub>	0.06
Chalcedony	-0.01
Siderite	-0.18

**Table 3.2:** Saturation indices of some minerals.

The keyword `temperature`, in abbreviated form `temp`, sets the temperature of the groundwater. The redox is automatically enabled when specifying the Eh value. As seen from the script, mildly reducing conditions prevail since the Eh is close to zero Volt. The Fe(III)/Fe(II) couple is observed to be in redox equilibrium and seems to be controlled by the paragenesis siderite/Fe(OH)<sub>3</sub> as indicated by the saturation indices of these minerals in Table 3.2. Calcite and Chalcedony (a Quartz polymorph) are also close to equilibrium as usual at low temperatures in such environment. Denitrification by pyrite oxidation, which is thermodynamically possible does not occur for unknown kinetic reasons. There is a redox disequilibrium state for nitrates which are so explicitly entered in the input script along with dissolved nitrogen. The apparent redox potential of the couple  $\text{NO}_3^-/\text{N}_2(\text{aq})$  is around 0.65 V: significantly far from the specified Eh value and hence from redox equilibrium.

### 3.4 Control of numerical parameters

A few keywords are provided to act on two numerical algorithms which are central in CHESS: the maximum number of iteration, and the precision of the Newton-Raphson algorithm, and the maximum number of iterations to find a stable assembly of solids in equilibrium with the aqueous solution. For instance, one can write in an input script:

```
maxit of newton-raphson = 2000
precision of newton-raphson = 1e-6
maxit of solids = 100
```

The default value of the above variables are respectively 1000,  $10^{-10}$  and 100. See Appendix C for further details.



## 4 Sorption and ion exchange

The previous chapter provided for an advanced introduction into modelling of geochemical equilibrium systems with CHESS. We have seen how colloidal and mineral solids can be included in the system, or how they can be created by precipitation. The surfaces of solids are in many cases reactive with respect to most metals occurring in earth's waters. And, the interface reactions between a solute and an inorganic (or organic!) surface are of major importance in geochemical systems. Metal sorption by mineral surfaces may significantly reduce the migration velocity of certain species. On the other hand, sorption onto mobile colloids may dramatically increase the apparent solubility and migration velocities of contaminants.

CHESS has been especially developed for reactions on colloidal surfaces. The methodology has been extended to all types of surfaces, colloidal, mineral, organic or inorganic, such that surface sites or functional groups are explicitly provided for all relevant species. In many cases, and especially with clay minerals, the *cation exchange* approach is a more convenient approach to model sorption, or in a more general sense the retention of metals since this process is beyond the single subject of surface reactions.

This chapter illustrates how CHESS accounts for surface complexation and cation exchange reactions. Also, a short section is devoted to the empirical  $K_d$  approach for sorption. A number of new keywords will be introduced. For a complete glossary of all available units and keywords, the reader should have a look at Appendix A and Appendix C of this manual.

### 4.1 Surface complexation

Surface complexation is generally considered to be the main interaction mechanism for *pure* systems, such as colloidal (hydr)oxides. Since the publication of the work of Dzombak and Morel (1990) on surface complexation of hydrous ferric oxide, most models nowadays use the double layer theory for the electrostatic correction term. CHESS makes no exception, but applies the formalism to other solid types (van der Lee 1997). The theory requires no additional parameters, which can be regarded as an advantage but also as a disadvantage, when one aims at finding the best fit to experimental data.

Our example concerns the modelling of a laboratory experiment about nickel sorption onto a colloidal suspension of hydrous ferric oxides (50 mg/l). This system is defined by the following script:

```
pH = 6.5
tot Na[+] = 5 mmol/l
tot Ni[2+] = 0.1 umol/l
tot ClO4[-] = 5 mmol/l

colloid >HFO = 50 mg/l
dissolution = disabled
```

Note that dissolution has been turned off. Indeed, hydrous ferric oxide is thermodynamically unstable with respect to e.g. hematite or other ferric phases as illustrated in the previous chapter. However, the colloids are expected to be kinetically stable given the experimental time scale, which justifies the act. Here is a snippet of the output file **CHESS.out**:

```
[snip]
Elemental concentrations (mol/l):
-----
species  aqueous    mineral  colloidal  organic    fixed      gaseous    total
H[+]     3.41e-07    0        0          0          2.762e-06  0          3.103e-06
Na[+]    0.005      0        0          0          0          0          0.005
Ni[2+]   9.445e-08  0        0          0          5.551e-09  0          1e-07
Cl04[-]  0.005      0        0          0          0          0          0.005
[snip]
```

The  $\text{Ni}^{2+}$  fixed fraction accounts for 5.5 % of the total concentration.

How does CHESS handle for surface complexation reactions in this example ? First of all, nothing else than the colloid is entered in the system. Indeed, it is the thermodynamic database which defines the type of reaction. The following snippet from the database defines a hydrous ferric oxide colloid (symbolized by >HFO) with, following the suggestion of Dzombak and Morel (1990), strong and weak sites:

```
>HFO {
  composition = 3 H2O, -3 H[+], 1 Fe[3+]
  logK = -2.1377
  vol.weight = 3113.9 kg/m3
  radius = 10 nm
  site >HFO(s)-OH {
    exch.cap. = 0.093 umol/m2
  }
  site >HFO(w)-OH {
    exch.cap. = 3.745 umol/m2
  }
}
```

A detailed explanation of how the database is formatted and which keywords are allowed and known by the model is provided in Appendix B. Here it is sufficient to note the definition of the sites *inside* the field of >HFO. Hence by including >HFO in the input script, the model automatically includes the sites in the system and remembers that they belong to >HFO, known as their *mother*-species. However, at this stage, the model does not yet know whether the sites will actually react with something, and according to which type of reaction: surface complexation or cation exchange. In the case of nickel, there is only one reaction defined in the database:

```
>HFO(s)-ONi[+] {
  composition = 1 >HFO(s)-OH -1 H[+] 1 Ni[2+]
  logK = 0.37
}
```

With such a composition, the surface charge changes with  $\text{Ni}^{2+}$  concentration and, accordingly, CHESS includes an electrostatic correction term and calculates an apparent

complexation constant. This constant may significantly differ from the intrinsic  $\log(K)$ 's provided by the database! Sometimes, it may be useful to turn off the electrostatic correction factor. This is easily done within CHESS. Simply type `electrostatics = disabled` in the input script, which disables the electrostatic correction term.

Coming back to our example, here is a second snippet of the output file **CHESS.out**:

```
[snip]
Concentrations and activities of relevant species
-----
name:                -----concentration-----  activity      act.coef.
                    (mol/l)      (g/l)          (mol/l)
ClO4[-]              0.005        0.49725        0.0046363      0.92727
Na[+]                0.005        0.11495        0.0046363      0.92727
>HFO(w)-OH           1.374e-05      1.374e-05      1.374e-05      1
>HFO(w)-OH2[+]       2.6962e-06     2.7175e-06     2.6962e-06     1
>HFO(w)-O[-]         1.6041e-06     1.6041e-06     1.6041e-06     1
>HFO(s)-OH           3.3698e-07     3.3698e-07     3.3698e-07     1
H[+]                 3.4103e-07     3.4373e-07     3.1623e-07     0.92727
Ni[2+]               9.4449e-08     5.5432e-06     6.9825e-08     0.73929
>HFO(s)-OH2[+]       6.6124e-08     6.6647e-08     6.6124e-08     1
>HFO(s)-O[-]         3.934e-08      3.934e-08      3.934e-08      1
OH[-]                3.449e-08      5.8659e-07     3.1982e-08     0.92727
>HFO(s)-ONi[+]       5.551e-09      3.202e-07      5.551e-09      1
NaOH(aq)             2.349e-11      9.3951e-10     2.3517e-11     1.0012
Ni(OH)2(aq)          7.1337e-15     6.6133e-13     7.1419e-15     1.0012
Ni2OH[3+]            6.07e-19       8.1573e-17     3.0763e-19     0.5068
Ni(OH)3[-]           2.4638e-19     2.7031e-17     2.2846e-19     0.92727
[snip]
```

At a pH of 6.5, the predominant surface species is >HFO(w)-OH. The speciation of the surface is strongly dependent on the pH, has shown for instance in van der Lee (1998). Another example of surface complexation, over a pH range this time, is discussed in Section 5.1 of this manual.

CHESS may simultaneously account for several types of surfaces, and for each surface type any numbers of sites. By example, organic colloids such as Aldrich Humics Acids, denoted in the database by >AHA, can be introduced in the script of the previous example to simulate the interaction of  $\text{Ni}^{2+}$  with a mixed colloidal suspension:

```
pH = 6.5
tot Na[+] = 5 mmol/l
tot Ni[2+] = 0.1 umol/l
tot ClO4[-] = 5 mmol/l

colloid >HFO = 50 mg/l
dissolution = disabled
organic >AHA = 5 mg/l
```

Here is a snippet of the corresponding output file:

```
[snip]
```

Elemental concentrations (mol/l):

species	aqueous	mineral	colloidal	organic	fixed	gaseous	total
H[+]	3.41e-07	0	0	0	2.766e-06	0	3.107e-06
Na[+]	0.005	0	0	0	0	0	0.005
Ni[2+]	1.817e-09	0	0	0	9.818e-08	0	1e-07
Cl04[-]	0.005	0	0	0	0	0	0.005
[snip]							

The fixed fraction of  $\text{Ni}^{2+}$  has this time significantly increased due to the strong affinity of the cation for the humic acids defined into the database.

## 4.2 Cation exchange

Cation exchange is a different type of reaction in which a cation from the solids is *exchanged* against an aqueous cation. It is usually considered to be the predominant interaction mechanism between solutes and clay minerals. The particularity of the reaction is the rule of charge conservation: the overall, net charge does not change with the reaction and is assumed to be nil. Mathematically, a cation exchange process can be compared to a surface complexation reaction without electrostatic correction. The two mechanisms are however of chemical distinct natures (see for instance Appelo and Postma (1993)). Swelling clays, by example, also exchange their interlayer cations in addition to cations coming from surface edge sites.

For instance, argillaceous rocks are considered as potential host media for underground repository of radioactive wastes. These rocks frequently contain an important proportion of the clay mineral illite, in pure or inter-stratified phases. The evaluation of the confinement properties of the illite fraction with respect to cesium is an issue of interest in safety assessment. We may illustrate this with the following (simplified) input script:

```

database = MyThermo.dbs
dissolution = disabled

pH = 7.4
tot Na[+] = 200 mmol/l
tot Cl[-] = 160 mmol/l
tot SO4[2-] = 20 mmol/l
tot Cs[+] = 10 umol/l

mineral Illite = 200 g/l, surface = 20 m2/g

```

The porewater is of Na-Cl-SO<sub>4</sub> type. The total aqueous concentration of  $\text{Cs}^+$  worths 10  $\mu\text{mol/l}$  before the interaction with illite. This mineral is set to a realistic content, and its dissolution is not expected to occur. Again, the actual cation exchange reaction is provided by the database since cation exchange data are intrinsic properties of a mineral. However, these data may significantly differ from one illite to another in function of the detailed mineralogy of the clay mineral, the rock type to which it belongs to, etc. For instance, the cation exchange capacity of illite varies from 20 to 50 meq/100g in the literature. Hence, we modified the CHESS database by introducing our own data, and

we renamed it as **MyThermo.tdb**. This new filename is specified in the input script by the keyword **database-filename** (**database** in short). The reader should refer to Appendix B of the manual for a full explanation of the database format. We defined the mineral illite as follows:

```
Illite {
  composition = -8 H[+], 0.25 Mg[2+], 0.6 K[+], 2.3 Al[3+],\
                3.5 SiO2(aq), 5 H2O,
  logK = -11.3859(0), -9.026(25), -5.555(60), -2.0472(100),\
          1.6128(150), 4.6923(200), 7.4468(250), 10.0976(300)
  site Illite(Na) {
    content = 1 Na[+]
    exch.cap. = 15 umol/m2
  }
}
```

Here, illite contains one site (a simplification, because the mineral also possesses surface complexation sites at the edges which are predominant at high pH) which exchanges  $\text{Na}^+$  with other cations. Note that we used a specific notation for cation exchange: **Illite(Na)** instead of **Illite-ONa**.

The cation exchange capacity is expressed in  $\mu\text{mol}/\text{m}^2$ . The number of cation exchange sites actually available in the system is calculated in function of the specific surface area and the total amount of illite given in the input script.

The actual cation exchange reaction is defined by the reaction in the database. In the case of an exchange of  $\text{Cs}^+$  against  $\text{Na}^+$ , this reaction states:

```
Illite(Cs) {
  composition = 1 Illite(Na), 1 Cs[+], -1 Na[+]
  logK = 2
}
```

The reaction conserves the charge of illite and the  $\log(K)$  corresponds by definition to the cation exchange constant.

Here is an excerpt of the output file:

[snip]

Concentrations and activities of relevant species

```
-----
name:                -----concentration-----  activity      act.coef.
                        (mol/l)      (g/l)      (mol/l)
Na[+]                0.1917      4.4071      0.14302      0.74605
Cl[-]                0.15732     5.5776      0.11737      0.74605
Illite(Na)           0.05999      1.3786      0.05999      1
SO4[2-]              0.014364     1.3799      0.0044499    0.30979
NaSO4[-]             0.005636      0.67098     0.0042047    0.74605
NaCl(aq)             0.0026751     0.15634     0.0028051    1.0486
Illite(Cs)           9.6722e-06     0.0010631   9.6722e-06   1
OH[-]                3.4051e-07     5.7912e-06  2.5404e-07   0.74605
Cs[+]                3.0907e-07     4.1077e-05  2.3058e-07   0.74605
```

H[+]	5.3362e-08	5.3783e-08	3.9811e-08	0.74605
CsCl(aq)	1.8762e-08	3.1588e-06	1.9674e-08	1.0486
HSO4[-]	2.263e-08	2.1967e-06	1.6883e-08	0.74605
NaOH(aq)	5.4952e-09	2.1979e-07	5.7622e-09	1.0486
HCl(aq)	9.5271e-10	3.4736e-08	9.99e-10	1.0486
H2SO4(aq)	6.4098e-19	6.2867e-17	6.7212e-19	1.0486

Elemental concentrations (mol/l):

species	aqueous	mineral	colloidal	organic	fixed	gaseous	total
H[+]	7.694e-08	0	0	0	0	0	7.694e-08
Na[+]	0.2	0	0	0	0.05999	0	0.26
Cl[-]	0.16	0	0	0	0	0	0.16
SO4[2-]	0.02	0	0	0	0	0	0.02
Cs[+]	3.278e-07	0	0	0	9.672e-06	0	
1e-05							
[snip]							

After equilibrium, the solution has clearly been depleted in aqueous Cs due to the Cs/Na exchange reaction. The Na exchangeable concentration is only slightly modified by the reaction since the total Cs concentration is relatively low. Due to the strong affinity of cesium for illite (the above Cs/Na exchange constant yields 100), the maximum threshold for cesium retention in our example is roughly about 60 mmol/l. Another application of cation exchange is presented in Section 5.4 of the manual.

### 4.3 The $K_d$ approach

The preceding sorption reaction were expressed with respect to one or several specific sites and species. In this way, the full complexity of the chemical reaction and competition effects is taken into account. But such a detailed and complex approach requires to introduce a rather large amount of experimentally obtained parameters and data — often not available. The empirical  $K_d$  approach therefore still remains very common practice in the field of contaminant transport and retention modelling.

By convention, the  $K_d$  coefficient is the distribution coefficient between the immobile and the mobile concentration of a species. The  $K_d$  does not account for site competition and saturation. It is not a thermodynamic reaction, and therefore not introduced in the thermodynamic database. And it does not refer to a specific species of an element, such as  $\text{CdOH}^+$ , but to the total aqueous concentration of that element, e.g.,  $\text{Cd}^{2+} + \text{CdOH}^+ + \dots$ . Due to these facts, the approach is not valid for conditions beyond those used for determining the  $K_d$  value.

A commonly encountered unit for  $K_d$  is the liter per kilogram. However, an alternative can be considered in terms of a non-dimensional  $K_d$ . It is the ratio between the immobile and the mobile concentration of a species, with both fractions expressed in mole per liter of solution. The non-dimensional  $K_d$  is thus the usual  $K_d$  (l/kg) times the solid concentration (kg/l).

Let us insert in the script of the previous example, the non-dimensional  $K_d$  for americium



measured by a batch experiment performed with the bulk argillaceous rock:

```
database = MyThermo.dbs
dissolution = disabled
```

```
pH = 7.4
tot Na[+] = 200 mmol/l
tot Cl[-] = 160 mmol/l
tot SO4[2-] = 20 mmol/l
tot Cs[+] = 10 umol/l
tot Am[3+] = 0.1 umol/l
```

```
mineral Illite = 200 g/l, surface = 20 m2/g
Kd of Am[3+] = 200
```

The  $K_d$  value is simply set by the keyword Kd. After running CHESS with this script, the output file contains something like this:

[snip]

Concentrations and activities of relevant species

```
-----
name:                -----concentration----- activity    act.coef.
                        (mol/l)      (g/l)      (mol/l)
Na[+]                0.1917      4.4071      0.14302    0.74605
Cl[-]                0.15732     5.5776      0.11737    0.74605
Illite(Na)           0.05999     1.3786      0.05999     1
SO4[2-]              0.014364     1.3799      0.0044499   0.30979
NaSO4[-]             0.005636     0.67098     0.0042047   0.74605
NaCl(aq)             0.0026751     0.15634     0.0028051   1.0486
Illite(Cs)           9.6722e-06     0.0010631   9.6722e-06   1
KdSite-Am            9.9502e-07     9.9502e-07   9.9502e-07   1
OH[-]                3.4051e-07     5.7912e-06   2.5404e-07   0.74605
Cs[+]                3.0907e-07     4.1077e-05   2.3058e-07   0.74605
H[+]                 5.3362e-08     5.3783e-08   3.9811e-08   0.74605
CsCl(aq)             1.8762e-08     3.1588e-06   1.9674e-08   1.0486
HSO4[-]              2.263e-08      2.1967e-06   1.6883e-08   0.74605
NaOH(aq)             5.4952e-09     2.1979e-07   5.7622e-09   1.0486
AmSO4[+]             1.8194e-09     6.1689e-07   1.3574e-09   0.74605
HCl(aq)              9.5271e-10     3.4736e-08   9.99e-10     1.0486
AmOH[2+]             1.6435e-09     4.2732e-07   5.0915e-10   0.30979
Am(OH)2[+]           3.3634e-10     9.317e-08    2.5092e-10   0.74605
Am(SO4)2[-]          2.3915e-10     1.0406e-07   1.7842e-10   0.74605
AmCl[2+]             2.1376e-10     5.9523e-08   6.6223e-11   0.30979
Am[3+]               7.2298e-10     1.7568e-07   5.1766e-11   0.0716
Am(OH)3(aq)          1.4847e-14     4.3653e-12   1.5568e-14   1.0486
H2SO4(aq)            6.4098e-19     6.2867e-17   6.7212e-19   1.0486
```

Elemental concentrations (mol/l):

```
-----
species  aqueous  mineral  colloidal  organic  fixed  gaseous  total
H[+]     7.694e-08  0        0          0        0      0        7.694e-08
Na[+]     0.2       0        0          0        0.05999  0        0.26
```

Cl[-]	0.16	0	0	0	0	0	0.16
S04[2-]	0.02	0	0	0	0	0	0.02
Cs[+]	3.278e-07	0	0	0	9.672e-06	0	1e-05
am[3+]	4.975e-09	0	0	0	9.95e-07	0	1e-06

[snip]

As expected, the ratio between the aqueous and fixed fractions of americium yields exactly 200. In fact, the  $K_d$  approach is really interesting for dynamic systems such as pollutants dissemination, provided a relatively simple chemistry for the polluting species. Note that the aqueous fraction of americium corresponds to a rather complex chemistry. The effects on sorption and solubility is probably not properly modelled by a single distribution coefficient.

## 5 Reaction Paths

In the previous chapters, you have seen how to apply CHESS to a *single* equilibrium calculation. But more often we are interested in how an aqueous species, a mineral or a surface evolves when one or more system variables are subject to change. Speciation diagrams, for example, illustrate which type of species is predominant at different Eh and pH ranges. In a general sense, a *reaction path* is a sequence of equilibrium states where one or several parameters are modified gradually.

Most of geochemical tools provide specific options to *bring* pH, species concentrations or temperature from an initial value to an end value: CHESS makes no exception, and even extends this option by providing for variation of different variables together up to the full simulation of water mixing or flushing. The CHESS specificities for reaction paths modelling is the topic of the present chapter. A number of new keywords will be introduced. For a complete glossary of all available units and keywords, the reader should refer to Appendix A and C of the manual.

### 5.1 Titration paths and speciation diagrams

One of the most common reaction paths is a *titration*, i.e. adding more and more of some recipe to the solution. CHESS provides a simple syntax for modifying the concentration or activity of a species: **bring**. For instance, let us consider the typical example of acid-base titration through the carbonate system which plays a central role in natural waters. With the following input-script,

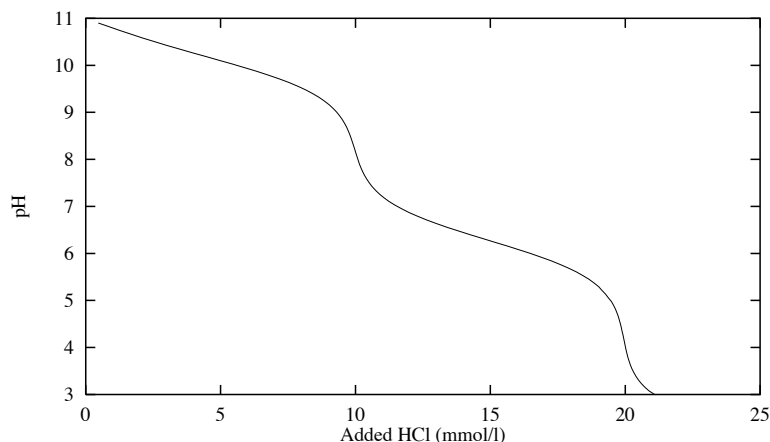
```
pH = 10.9
tot Na[+] = 20 mmol/l
tot C03[2-] = 10 mmol/l
tot Cl[-] = 1e-25 mol/l

bring pH to 3
balance on Cl[-]
precipitation = disabled

select Cl[-], pH, C02(aq), HC03[-], C03[2-] in mmol/l
```

CHESS will compute the titration curve of sodium carbonate,  $\text{Na}_2\text{CO}_3$ , at a concentration of  $10^{-2}$  mol/l by the strong acid HCl. The initial solution is defined by the first four lines. The equilibrium pH of that solution has been calculated before with another CHESS run. The next lines set the titration path parameters through the keyword **bring**. In the last line, the variables to be recorded during the modelling are selected and written in columns in an output file, by default **CHESS.res**, which can be visualized with any graphical software. Another filename may be specified with the keyword **path-filename**. In our example, the header of the path-filename looks like this:

```
# Created by CHESS version 2.4, patch level 1
# CHESS.res
```



**Figure 5.1:** Titration of  $\text{Na}_2\text{CO}_3$  (10 mmol/l) by HCl.

```
# Mon Dec 21 15:58:45 1998
```

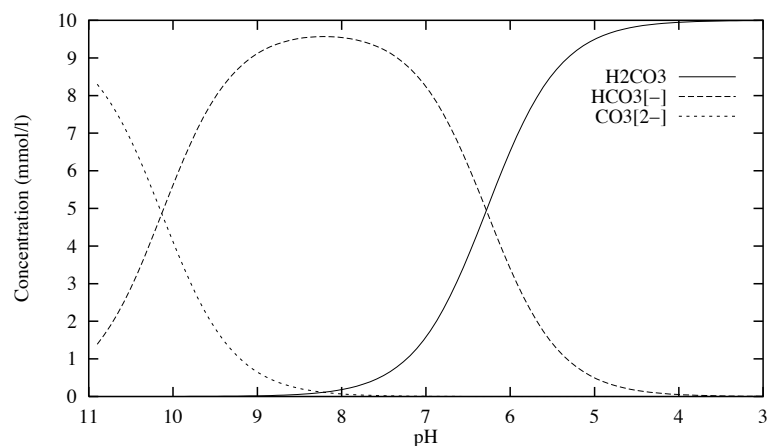
```
# column 1: Cl[-]                scaled by 1000
# column 2: pH
# column 3: CO2(aq)              scaled by 1000
# column 4: HCO3[-]             scaled by 1000
# column 5: CO3[2-]             scaled by 1000
```

```
9.97625e-23 10.9      2.22068e-05 1.15709    8.52811
0.419596   10.9101   3.13833e-05 1.35982    8.32758
0.817488   10.8302   4.41837e-05 1.59184    8.09805
1.21988    10.7503   6.19296e-05 1.85507    7.83767
[snip]
```

The first lines are "commented out" by the common comment-character '#', recognized by many graphical packages and Unix utilities such as **awk**. The *scaled by* comment is a consequence of the unit *mmol/l*, which we added to the select comment. In general, to set different units for different items, several lines of **select** must be introduced. Figure 5.1 shows the calculated titration curve. As illustrated in the previous chapters, the general output file (by default **CHESS.out**) provides detailed informations on the initial and final states, but also some other informations on the reaction path sequence itself such as possible dissolution or precipitation events.

The Figure 5.2) illustrates an important application of titration-like diagrams, the *speciation diagrams*. You easily recognized the well known species distribution of the carbonate system as pH shifts from alkaline to more acidic conditions. A speciation diagram can be drawn for any species under any chemical changes, such as for instance the complexation of uranyl ions by carbonate ligands. This example is reported in Fig. 5.3 based on the following input script:

```
pH = 8
tot UO2[2+] = 1e-6 mol/l
```



**Figure 5.2:** Speciation of the carbonate system during the titration.

```
tot HCO3[-] = 1e-6 mol/l
bring HCO3[-] to 1e-1 mol/l, log
samples = 200
select HCO3[-], *UO2* in mol/l
```

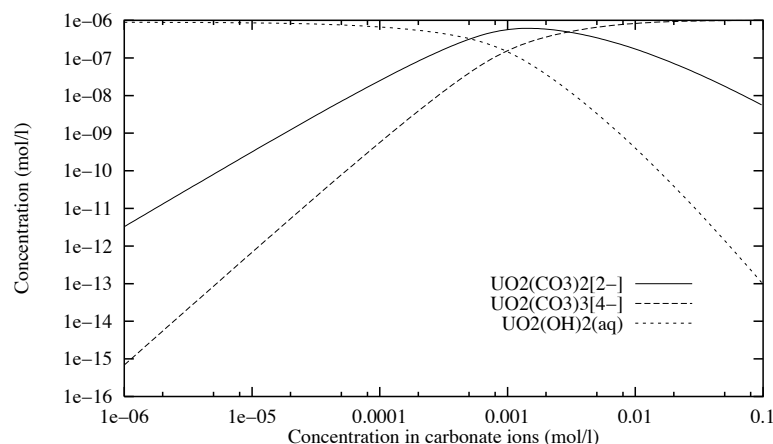
The **log** option of the keyword **bring** enables logarithmic steps. The keyword **samples** allows to modify the number of samples written to **CHESS.res** (100 by default). The wild-character “\*” is used to select all the species including the string of characters “UO2” in their writing (UO2[2+], UO2CO3(aq), etc.). The competition effect of carbonate complexation towards hydroxyl complexation is enhanced as the carbonates aqueous concentration increases, finally leading to the predominance of  $\text{UO}_2(\text{CO}_3)_3^{4-}$  which stabilizes uranium and favors its transport in groundwater.

A speciation diagram may also include one or several solid species. For instance, the next input script stands for the evolution of the fixed fraction of copper and selenium onto goethite colloids in a contaminated water as the pH changes:

```
pH = 4
tot Na[+] = 0.01 mol/l
tot Cl[-] = 0.01 mol/l
tot SeO4[2-] = 5 umol/l
tot Cu[2+] = 5 umol/l
colloid >HF0 = 1.0 g/l, surface = 200 m2/g

bring pH to 8.5
balance on Na[+]
precipitation = disabled

select pH
select charge{>HF0} in uC/cm2
select fixed{SeO4[2-]}, fixed{Cu[2+]} in umol/l
```



**Figure 5.3:** Speciation diagram of the complexation of uranyl ions by carbonate ligands.

The results are given in Figure 5.4. The special item `charge{>HF0}` is used to create a column with the surface charge of species `>HF0` during the reaction path. When the pH of the polluted water evolves towards an alkaline water, the colloidal surface switches from a positive to a negative charged state (the functional groups change from a major `>Goethite-OH2+` to a major `>Goethite-O-` population (van der Lee 1998)). Consequently, the selenium, of which major aqueous species is anionic, desorbed; whereas the cation  $\text{Cu}^{2+}$  is increasingly fixed by colloids.

## 5.2 Polythermal reaction paths

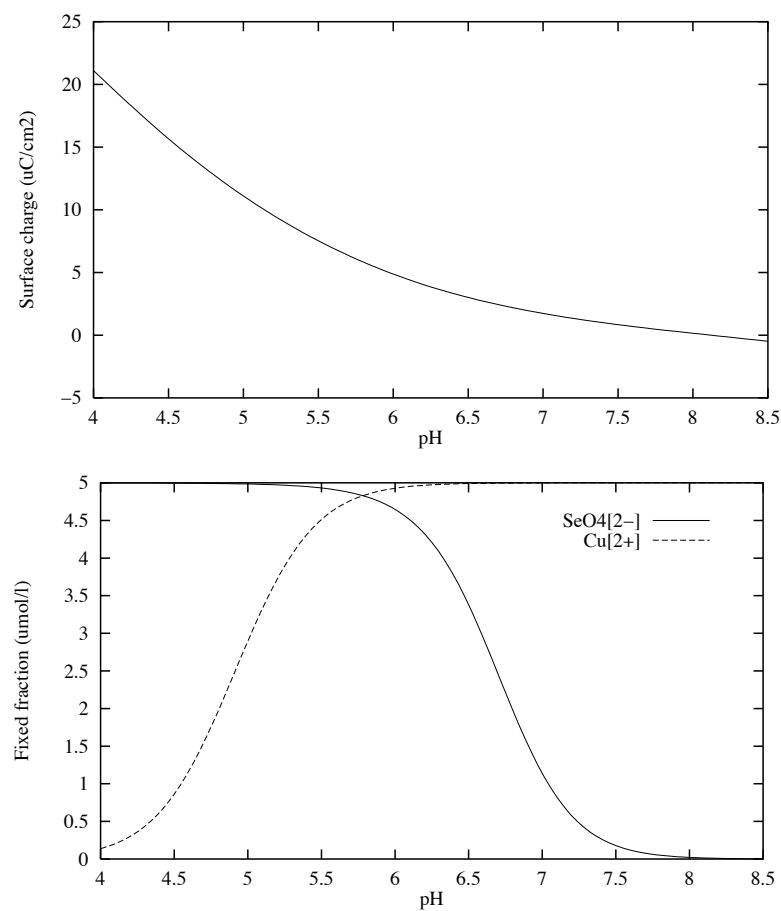
From a pure algorithmic point of view, the modelling of a reaction path driven by *temperature* is similar to the titration paths of the former section. However, in practical studies of mineral evolutions under thermal stresses, it is often individualized in terms of polythermal reaction paths. Temperature is an intensive variable, and all the thermodynamic related processes of an aqueous geochemical system are temperature dependent.

Here is a short input-script which simulates a common daily life problem: calcareous deposits in your shower ...

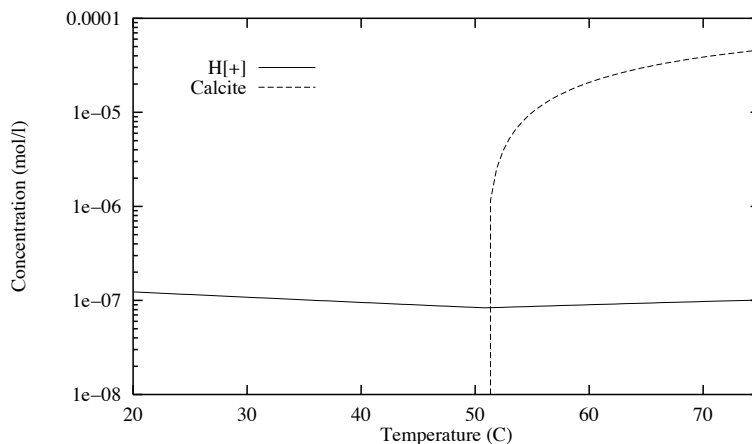
```
exclude minerals, colloids
include Calcite
```

```
temp = 20 C
fug C02(g) = 1e-3
pH = 7
tot Ca[2+] = 3e-2 mol/l
```

```
bring temp to 75 C
free pH
```



**Figure 5.4:** Evolution with respect to pH: a) electrical surface charge of HFO colloids, b) fixed fractions of Cu and Se.



**Figure 5.5:** Evolution of proton and Calcite concentrations with temperature.

```
select temp in C
select H[+], Calcite in mol/l
```

The core of the polythermal reaction path is again related to the **bring** keyword which involves this time the temperature. The results of this simulation are shown in Figure 5.5. As the temperature rises, the saturation indices of calcite increases: hence its solubility decreases and calcite starts to precipitate. This *retrograde* behaviour of a mineral solubility with temperature is surprising, and is due to the indirect effect of  $CO_2$  degazing which slightly shifts the pH towards alkaline values.

### 5.3 Using mix-with

The reaction paths discussed so far were governed by the changes of one single variable. CHESS generalizes the notion of titration paths by allowing the evolution of a *initial* solution with regard to a second geochemical *subsystem*. One of these generalized reaction path is provided for by the keyword **mix-with**, which enables to simulate progressive mixing of two different waters. The keyword is followed by the definition of the subsystem, where everything within { and } is considered to form part of it.

Basically, CHESS solves first for the equilibrium state of the initial system, then for the subsystem. The subsystem is linearly added to the initial system in a number of steps defined by **samples** (100 by default). At the end, the two waters are totally mixed. The **mix-with** keyword is especially useful for complex geochemical systems, where two significantly different waters are mixed. The final result is often far from a pure conservative mixture of both fluids, when precipitation, dissolution or adsorption processes take place. CHESS knows how to handle heterogeneous systems, i.e. the definition of different species in the initial system and in the mix-with subsystem. Basically, all usual CHESS keywords may be used in the subsystem.

It is important to realize that **mix-with** mixes both systems entirely, i.e. all phases



(mineral, gaseous, colloidal) are progressively added to the initial system. It is, however, sometimes useful to mix only the *mobile* fraction of the mix-with subsystem. The mobile fraction is defined as the fraction which is "displaceable" by a process such as hydrological flow, hence all species but minerals and species sorbed to these minerals. Note that colloids form part of the mobile fraction! In order to mix with mobile fractions only, the `mix-with` should be used with an optional keyword, `mobile-fraction`.

Let us illustrate this new keyword with an example, where we are interested in predicting the barium solubility in water flowing from mine wastes to a limestone aquifer with a mixing ratio of 1:9. The wastes originate from an acidic treatment of ore deposits and the corresponding seepage water is strongly enriched in barium. The following (simplified) input-script simulates the water mixing:

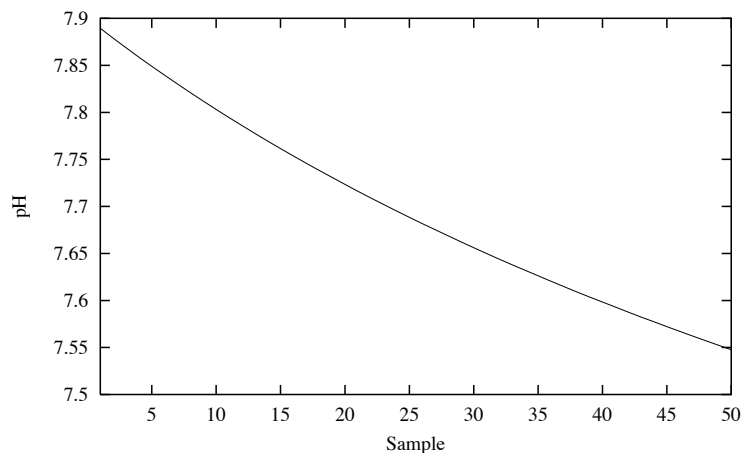
```
temp = 10 C
volume = 0.9 l
pH = 7.9
mineral Calcite = 1 kg/l

mix-with mobile-fraction {
  temp = 18 C
  volume = 0.1 l
  pH = 2.0
  tot Na[+] = 2 mg/l
  tot Ba[2+] = 2.5 mg/l
  tot NO3[-] = 700 mg/l
  balance on Na[+]
}

balance on HCO3[-]
samples = 50
select sample, pH
select aqueous{Ba[2+]}, mineral{Ba[2+]} in mg/l
```

The limestone water system is defined by the four first lines. The `mix-with` field comes next. The keyword `volume` is used in both systems in order to set the correct mixing ratio. By default, the volume is set to one liter for both systems. The temperature during the mixing is calculated on the assumption of identical heat capacities for each fluid. The electroneutrality of the solution is warranted by a `balance` requirement on the main anions. As previously, the keyword `samples` allows to vary the number of mixing steps. The last two lines lead to the recording, for each step, of pH and of the total aqueous and mineral concentrations of barium expressed in mg/l.

The results are reported in Figure 5.6 and Table 5.1. This example nicely shows the usefulness of the `mix-with` option. The final pH, for instance, differs from the value one would obtained from a pure conservative mixing due to the buffer effect of calcite. The barium solubility is controlled along the mixing path by witherite, which is a barium carbonate mineral poorly soluble in neutral pH conditions. The barium concentration in the aquifer is kept one thousand times lower than in the polluted water. But, although controlled, the total aqueous concentration of barium is not constant over the full range of the simulation due to the decrease in  $\text{CO}_3^{2-}$  concentration with pH.



**Figure 5.6:** Evolution of pH during the mixing.

	Wastes	Aquifer	Mixture
aqueous fraction (mg/l)	2.5	0.	0.002
$\sum$ mineral fraction (mg/l)	0.	0.	0.248

**Table 5.1:** Aqueous and mineral fractions of barium before and after the mixing of waters.

## 5.4 Using flush-with

The flushing process is a second type of generalized reaction path implemented in CHESS. The **flush-with** option tracks the evolution of a system through which fluids migrate or partially mix with the initial solution. The flush model is fruitful to simulate the chemical effects on soils or rocks of fluid circulations, as it occurs by example, with contaminant plumes or hydrothermal events.

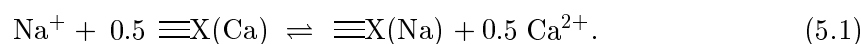
The volume of the flushing solution may be equal to or different from the volume of the mother system. CHESS proceeds as followed:

1. the mobile fraction of the mother system is partly replaced by the flushing solution, and a new equilibrium state is computed<sup>1</sup>;
2. the mobile fraction of the new system is itself totally or partly replaced by the flushing solution, and a subsequent new equilibrium state is computed;
3. the scheme is iteratively repeated 100 times unless specified otherwise with keyword **samples**.

<sup>1</sup>The volume of the mother solution which is replaced at each sample is equal to the ratio between the volume of the flushing solution and the total number of samples. The volume of replacement should be  $\leq$  than the volume of the mother solution.

The `flush-with` keyword is commonly used with the optional *mobile-fraction* argument, which allows for flushing with the mobile fraction of the subsystem only.

Let us consider the pollution of a coastal fresh water aquifer by salt water (see for instance Appelo and Postma (1993)). As a result of calcite dissolution, the waters of the aquifer are dominated by  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  and the cation exchangers present dominant  $\text{Ca}^{2+}$  adsorbed populations. In sea water, the major ions are  $\text{Na}^+$  and  $\text{Cl}^-$ . When sea water intrudes the aquifer, an exchange of cations occurs. This reaction can be written in terms of the Gaines-Thomas convention as follows:



Such a reaction path can be modeled by the following input-script:

```
database = MyThermo.dbs
exclude colloids

volume = 1 l
pH = 8
tot Na[+] = 0.01 mmol/l
mineral Quartz = 800 g/l
mineral Calcite = 150 g/l
mineral Clay = 50 g/l, surface = 15 m2/g
balance on HC03[-]

flush-with mobile-fraction {
  volume = 5 l
  pH = 7
  tot Na[+] = 480 mmol/l
  tot Ca[2+] = 10 mmol/l
  tot Cl[-] = 500 mmol/l
}

select sample
select aqueous{Na[+]}, aqueous{Ca[2+]} in mmol/l
select fixed{Na[+]}, fixed{Ca[2+]} in mmol/l
```

The first two lines concern the selection of the dataset. As it often occurs for applications to natural (and therefore complex) systems, the cation exchange reactions are not characterized with respect to specific mineral phases but rather with respect to an average bulk material, corresponding to the global response of the clay and organics fractions of the soil or rock. In our example, we have introduced a generic clay mineral, *Clay*, in the database with a new cation exchange site. Here are the relevant parts:

```
minerals {
...
  Clay {
    vol.weight = 2500 kg/m3
    site Clay(Ca) {
      content = Ca[2+]
      exch.cap. = 10 umol/m2
```

```

        molew. = 40.078
    }
}
...
}
surface-sites {
...
    Clay(Na) {
        composition = 0.5 Clay(Ca), -0.5 Ca[2+], 1 Na[+]
        logK = -1.16
    }
...
}

```

The new database file has been renamed **MyThermo.tdb**. The exchange capacity is expressed in  $\mu\text{mol}/\text{m}^2$  similarly to the surface complexation data<sup>2</sup>. The  $\log K$  corresponds to the cation exchange constant

Note that, in CHESS, the activities of the fixed ions are calculated with respect to the usual standard state of 1 mol/kg of  $\text{H}_2\text{O}$ , and not with respect to the solid like in the Gaines-Thomas convention (van der Lee 1998). In the case of Eq. 5.1, the transcription of a Gaines-Thomas selectivity coefficient,  $K^{GT}$ , into a cation exchange constant,  $K$ , is

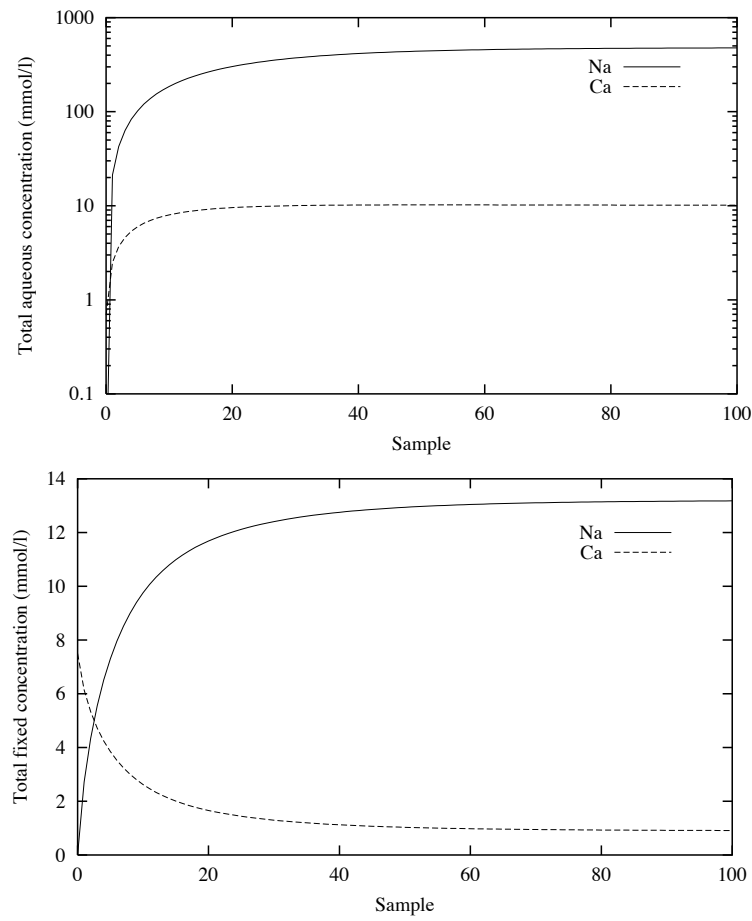
$$K = K^{GT} \sqrt{2\sigma A_s S}.$$

where  $\sigma$  denotes the exchange capacity of the clay (only of site  $\beta\text{Clay}(\text{Ca})$ ),  $A_s$  is the specific surface and  $S$  denotes the concentration of Clay. The effects of salt water intrusion is illustrated in Figure 5.7. The bicarbonate calcium water shifts towards a Na-Ca-Cl water type. The incoming sodium cations replace the exchangeable calcium ions, which are released in solution. Note that the total aqueous concentration of  $\text{Ca}^{2+}$  remains controlled by calcite during the flushing process.

The **flush-with** option is only a first step towards the simulation of the true hydrogeological dynamic. The correct modelling of a pollutant plume propagation in an initial system requires, as far it is technically possible, a transport model coupled with geochemistry (see van der Lee (1998), for example).

---

<sup>2</sup>In our example, the exchange capacity of  $\text{Clay}(\text{Ca})$  has been set to 10  $\mu\text{mol}/\text{m}^2$ ; hence 20  $\mu\text{eq}/\text{m}^2$  or  $(20 * 15)$   $\mu\text{eq}/\text{g}$ .



**Figure 5.7:** Evolution of sodium and calcium total aqueous and fixed concentrations during the flushing.



## 6 Kinetics of dissolution and precipitation

So far, all the simulations carried out by CHESS were based on a thermodynamic equilibrium approach. It is well recognized, however, that many reactions are *kinetically controlled* over the simulated time range. CHESS deals with kinetics of dissolution and precipitation reactions both for mineral and colloidal species. These mechanisms can be understood in terms of a hydrodynamic contribution function of the diffusive and convective transport of reactive species and products, and of a contribution related to the sorption and chemical reactions occurring at the solid/solution interface. The kinetic law introduced in CHESS refers to the second contribution. A full approach of a kinetic reaction calls for the use of a true transport model coupled with geochemistry. However, in a first approximation, CHESS can already introduce kinetics for hydrodynamic systems through the flushing or mixing options.

In this chapter, we learn how to deal with a panel of kinetic reactions using CHESS. A number of new keywords will be introduced. The complete sets of available units and keywords are given in Appendix A and C.

### 6.1 Kinetic laws

The mechanisms involved in kinetic dissolution or precipitation of a solid are generally complex. For instance, the precipitation of a mineral depends on the nucleation process and the saturation state of the mineral with respect to the solution. The saturation state of a mineral  $M_pX_q$ , is defined by

$$\Omega = ([M^{q+}]^p[X^{p-}]^q)/K_s, \quad (6.1)$$

with  $[M^{q+}]$  the activity of the ion  $M^{q+}$  and  $K_s$  the solubility constant.

The saturation state is also used as an indicator of the tendency for a mineral to dissolve. The higher the undersaturation of a mineral the faster its dissolution. The saturation state is thus a variable taken into account in the basic kinetic law implemented in CHESS to compute the variation of the quantity of a given mineral with respect to time:

$$\frac{d(S_j)}{dt} = (A_vk)_j(\Omega^p - 1). \quad (6.2)$$

The rate constant of the reaction is denoted by  $k$ . The reaction rate is supposed to be proportional to the volumic surface area of the mineral,  $A_v$ , expressed in  $\text{m}^2/\text{m}^3 \text{ H}_2\text{O}$ . When  $(\Omega^p - 1) > 0$ , the mineral precipitates, whereas for  $(\Omega^p - 1) < 0$ , the mineral dissolves. By default, the power  $p$  is set to unity.

### 6.2 Calcite dissolution

Let's illustrate the impact of this kinetic law with a simulation of calcite dissolution under laboratory controlled conditions. Here is the CHESS input script:

```

pH = 7.5
fug CO2(g) = 3e-4
tot Na[+] = 0.04 mol/l
tot Cl[-] = 0.04 mol/l
balance on Cl[-]

mineral Calcite = 100 g/l, surface = 50 cm2/g
kinetics of Calcite {
  rate = 1.4e-9 mol/cm2/s
  power of omega = 0.5
}

bring time to 20 min
select time in min
select aqueous{Ca[2+]}} in mmol/l,
select SI{Calcite}

```

The script is structured in three parts. The first one sets the chemistry of the solution before the addition of calcite. The partial pressure in  $CO_2$  and the pH are kept constant (buffered) all along the experiment. This choice reduces the number of free parameters during the experiment. The dissolution of carbonate minerals is indeed dependent on proton concentration and dissolved  $CO_2$ . By default, room temperature (25 °C) is assumed.

The second part provides the calcite concentration, specific surface, experimental rate constant and the power of  $\Omega$  within the *kinetics* field. The **rate** keyword (which should be defined imperatively) is expressed in mol/cm<sup>2</sup>/sec. As usual in CHESS, any equivalent units may be used (see Appendix C). The definition of the surface is similar to what have been presented previously for sorption in Chapter 3. A specific surface of 50 cm<sup>2</sup>/g corresponds to millimeter-size crystals. Finally, in the third part, the keyword **bring** set the duration of the simulation along with the selection of the parameters to be recorded. The overall simulation can be regarded as a reaction-path under time evolution.

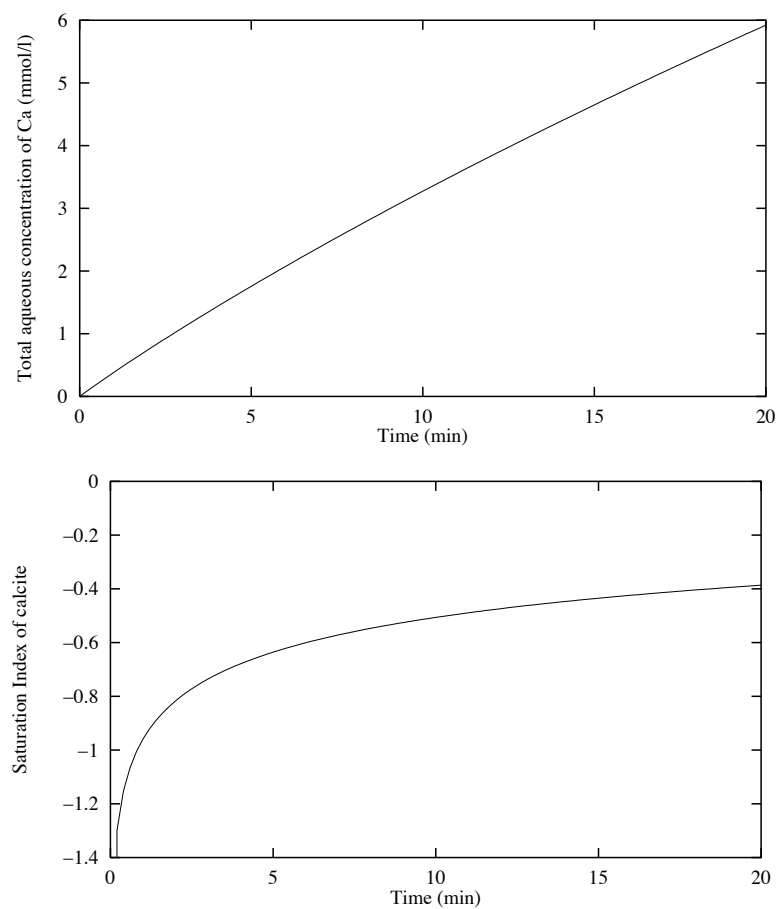
The results of the simulation are reported in Figure 6.1. The saturation index of calcite shows a quick increase the very first minutes followed by a flat evolution. The rate of  $Ca^{2+}$  release in solution remains constant during the experiment. This is the result of a system where pH and  $pCO_2$  are buffered, i.e., they remain constant in time.

It would have been different if the pH and  $pCO_2$  were *not* buffered, but free to vary as the solution evolves. CHESS allows to set one or several imposed species free after the initial equilibrium calculations. This is obtained by adding

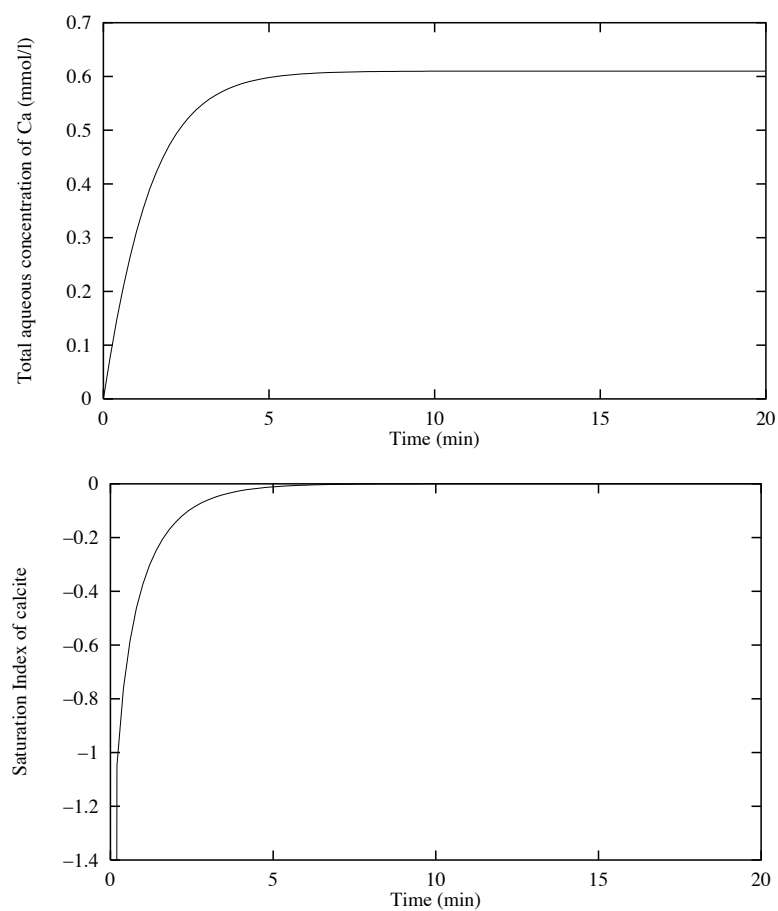
```
free pH, CO2(g)
```

to the input script. Figure 6.2 shows the result for the script with the **free pH, CO2(g)** statement. The saturation index rapidly becomes zero and the dissolution stops. The calcite dissolution shifts the fluid towards more alkaline conditions where calcite solubility is lower.





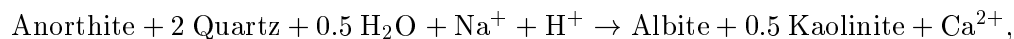
**Figure 6.1:** Kinetic modelling of calcite dissolution under buffered pH and  $p_{CO_2}$  conditions.



**Figure 6.2:** Kinetic modelling of calcite dissolution under free pH and  $p_{CO_2}$ .

### 6.3 Plagioclase albitization

As a second example of application of the basic kinetic law, we will consider the geochemical problems of sandstone diagenesis in contact with saline fluids for a medium temperature range. The reaction under consideration is:



which describes the process of plagioclase albitization. Here is the related (simplified) input script:

```
exclude minerals, colloids
include Albite, Anorthite, Kaolinite, Quartz
temp = 80 C
pH = 7.8
tot Ca[2+] = 13 mmol/l
tot Na[+] = 530 mmol/l
tot Cl[-] = 560 mmol/l
balance on Cl[-]
conc Kaolinite = 50 g/l

mineral Albite = 100 g/l, surface = 200 cm2/g
kinetics of Albite {
  rate = 1e-15 mol/cm2/s
}
mineral Anorthite = 100 g/l, surface = 200 cm2/g
kinetics of Anorthite {
  rate = 1e-15 mol/cm2/s
}
conc Quartz = 750 g/l, surface = 200 cm2/g
kinetics of Quartz {
  rate = 5e-16 mol/cm2/s
}

bring time to 1500 years
free pH
select time in years
select pH
select SI{Albite}, SI{Anorthite}, SI{Kaolinite}, SI{Quartz}
select Albite, Anorthite, Kaolinite, Quartz in g/l
report SI downto -5
```

The input script is again divided in three parts. The chemistry of the solution and temperature is set in the first part. The initial fluid is assumed to be in equilibrium with respect to kaolinite, since the kinetic of kaolinite is much faster relatively to the other minerals.

The second part deals with the kinetic parameters of albite, anorthite and quartz. An average value of specific surface is introduced for all minerals of which proportions are representative of a common sandstone. The last part specifies the duration of the experiment and the parameters to be recorded. The pH is set free, i.e., its value is not imposed after the initial equilibrium calculations. The command `report SI downto -5` decreases the threshold for reporting of mineral saturation indices ( $-3$  by default).

The results of the kinetic modelling are reported in Figure 6.3. Once the kinetics starts, the minerals anorthite and albite, which are respectively undersaturated and oversaturated with respect to the fluid, dissolve and precipitate.

---

When a mineral which should precipitate under kinetic constraints does not exist in the initial system, a volumic surface has to be specified in  $\text{m}^2/\text{l}$  or equivalent units to initiate the kinetic reaction (simulating nucleation processes or crystal growths on other solids). For instance, the command `mineral Chalcedony = 0 g/l, surface = 1 m2/l` will allow the precipitation of chalcedony if relevant. Note that CHESS does not vary the volumic surface with respect to the mass of the solid, contrary to the specific surface.

---

simultaneously. It is worth noting that quartz, which was initially in equilibrium, also dissolves due to the relative differences in the kinetic rates of each minerals. During the reaction-path, there is an alkalization of the fluid and the pH globally increases (the pH evolution is however more complex than in the previous example). At the end of the simulation, all the minerals have reached thermodynamic equilibrium.

## 6.4 Temperature dependence

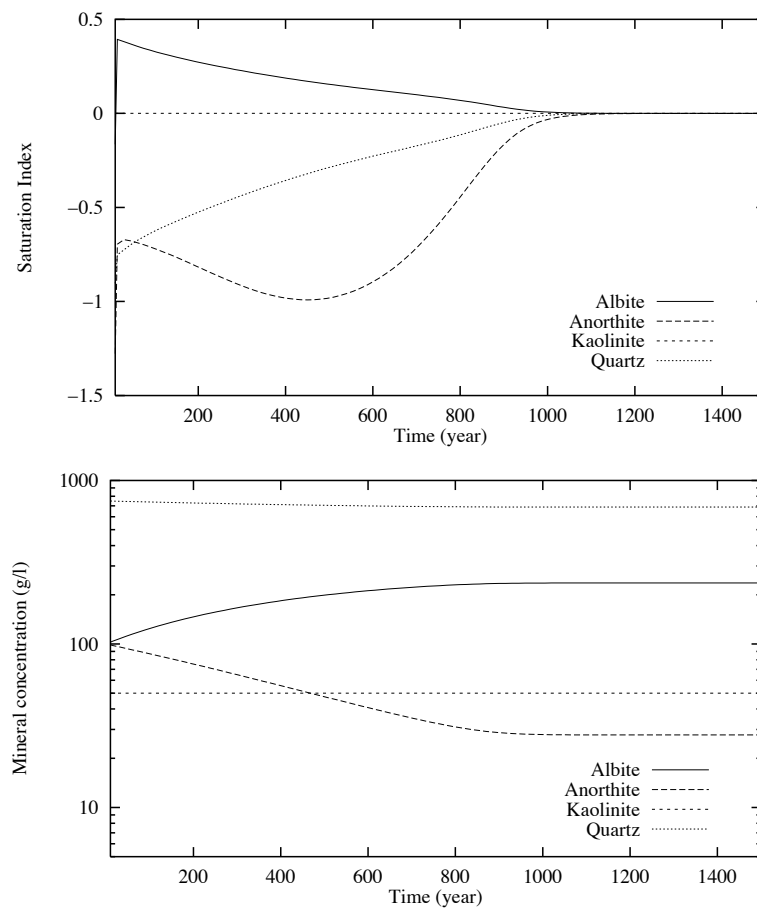
An Arrhenius-like law is implemented in CHESS to take into account the (often strong) dependence of a kinetic relation with *temperature*:

$$k = A \exp \left( \frac{-E_A}{RT} \right), \quad (6.3)$$

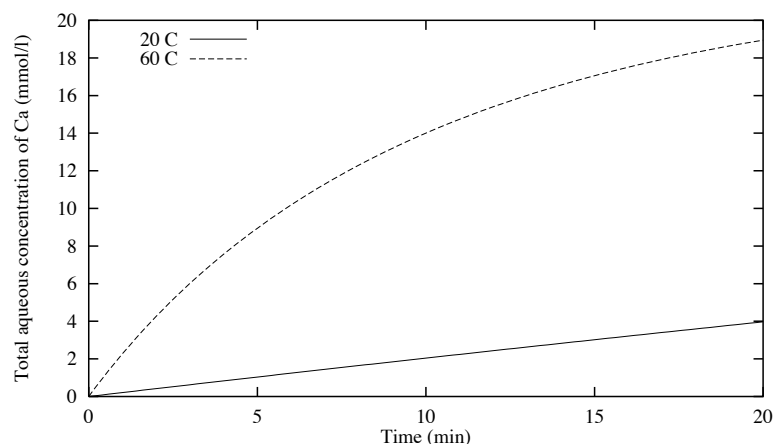
where  $A$  is a pre-exponential factor,  $E_A$  is the apparent activation energy (in J/mol),  $R$  is the perfect gas constant, and  $T$  is the absolute temperature in  $^{\circ}\text{K}$ . What would be the temperature effect on the calcite dissolution discussed in the first example ? Here is the input script to model such a reaction at  $60^{\circ}\text{C}$ :

```
temp = 60 C
pH = 7.5
fug CO2(g) = 3e-4
tot Na[+] = 0.04 mol/l
tot Cl[-] = 0.04 mol/l
balance on Cl[-]

mineral Calcite = 100 g/l, surface = 50 cm2/g
kinetics of Calcite {
```



**Figure 6.3:** Kinetic modelling of plagioclase albitization at 80 °C.



**Figure 6.4:** Total aqueous concentration in calcium during calcite dissolution at 20 and 60 °C.

```
rate = 9.9e-10 mol/cm2/s at 25 C
arrhenius-energy = 5e4 J/mol
}
```

```
bring time to 20 min
select time in min
select aqueous{Ca[2+]} in mmol/l
select SI{Calcite}
```

The script is very similar to the first one, but this time the temperature of the solution is explicitly set (60 °C). Within the `kinetics` field, one notes two modifications:

1. the temperature related to a known rate constant is provided;
2. the value of the apparent activation energy is introduced through the keyword `arrhenius-energy`.

The total aqueous concentration in  $\text{Ca}^{2+}$  during calcite dissolution at 20 and 60 °C is plotted in Figure 6.4. The dissolution of minerals generally increases with temperature (they become less stable). Indeed, calcite dissolution at 60 °C is roughly 10 times faster compared to the process at 20 °C, at least at the start of the simulation.

## 6.5 Catalyzing and inhibiting effects

It is a common observation that the kinetic rate of a given reaction can strongly be affected by the presence of species which do not participate, from a thermodynamic balance point of view, to the reaction. Such species, which are often found in weak concentrations, are said to have a *catalyzing* effect when they speed up the reaction,

and an *inhibiting* effect when they slow down the reaction. In our problem of solid dissolution or precipitation, such effects may be taken into account through the following generalization of the basic kinetic law (Eq. 6.2):

$$\frac{d(S_j)}{dt} = (A_v k)_j \prod_i [C_i]^{a_{ij}} (\Omega - 1). \quad (6.4)$$

The activity of a catalyzing species will be brought to a positive power, whereas the activity of an inhibiting species will be brought to a negative power.

Here comes again our calcite example. Not because it is the only studied species (the literature offers a wide range of kinetics data), but because it helps us to illustrate the greater variability of the kinetics parameters compared to the thermodynamic ones. Here is a script which illustrates the use of a catalyzing species:

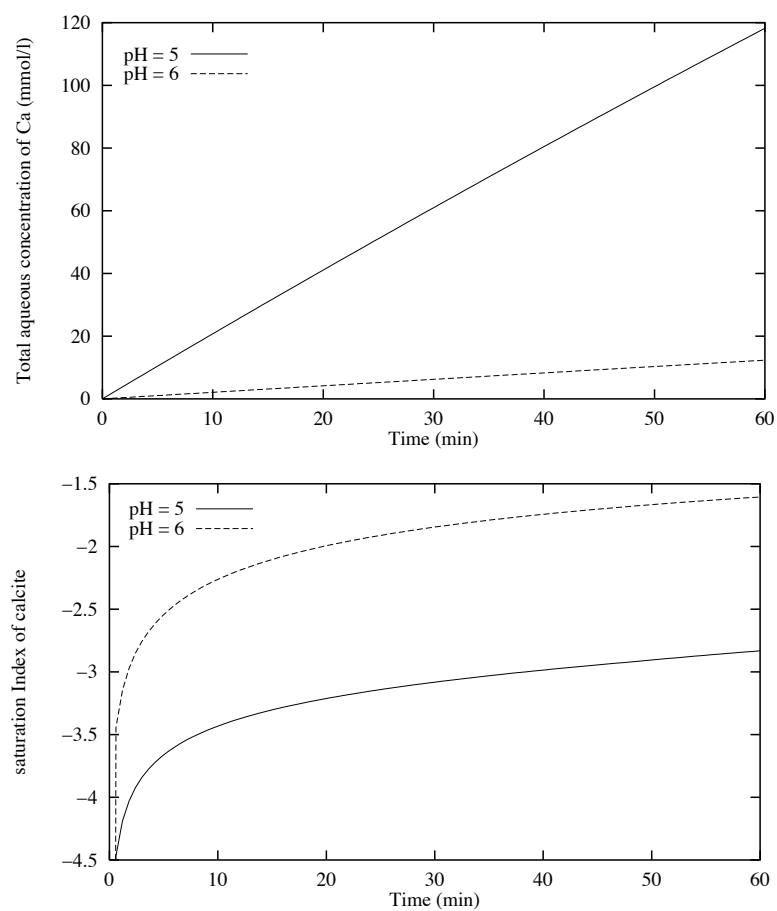
```
pH = 6.0
fug CO2(g) = 0.02
tot Na[+] = 0.01 mol/l
tot Cl[-] = 0.01 mol/l
balance on Cl[-]

mineral Calcite = 100 g/l, surface = 50 cm2/g
kinetics of Calcite {
  rate = 0.0007 mol/cm2/s
  power of H[+] = 1
}

bring time to 60 min
select time in min
select aqueous{Ca[2+]}} in mmol/l
select SI{Calcite}
```

The fugacity of CO<sub>2</sub>(g) is this time set at a value higher than the average atmospheric one, but is still buffered. The pH is slightly acidic and remains fixed during the whole experiment. The catalyzing effect of H[+] is introduced through the keyword **power** within the **kinetics** field. The absolute value of the rate constant has dramatically changed in comparison to the first example (due to its dependence on the dissolved CO<sub>2</sub>(g), and the consideration of the proton effect). Note that more than one **power** declaration is allowed (in fact, the number of species is unlimited), provided they are specified on separate lines.

The results of the simulation are shown in Figure 6.5 for two pH values. The dissolution rate of calcite increases of one order of magnitude when the pH decreases one unity, as it is expected from equation (6.4).



**Figure 6.5:** Kinetic modelling of calcite dissolution under acidic conditions for  $\text{pH} = 5$  and 6.



## 6.6 Hydrodynamic systems

Any kinetic constraints on the dissolution or the precipitation of solids may be introduced in a mixing or flushing reaction path. This is an interesting feature if you are interested in studying natural, *dynamic* systems, such as transport of contaminants in an aquifer.

In order to illustrate this ability of CHESS, consider an experiment devoted to the characterization of the dissolution rate of amorphous uranium dioxides in a flow reactor kept under strongly reducing conditions. We propose a combination of kinetics and a flushing process to simulate the experiment. It is assumed that the kinetic parameters have been obtained previously from batch experiments. A input script to simulate the experiment could be:

```
precipitation = disabled
redox = disabled of ClO4[-]
time = 180 days
temp = 20 C

volume = 0.1 l
pH = 6
Eh = -0.2
tot Na[+] = 5 mmol/l
tot ClO4[-] = 5 mmol/l
mineral UO2(am) = 10 g/l, surface = 100 cm2/g
kinetics of UO2(am) {
    rate = 1e-12 mol/cm2/s
    power of H[+] = 0.5
}

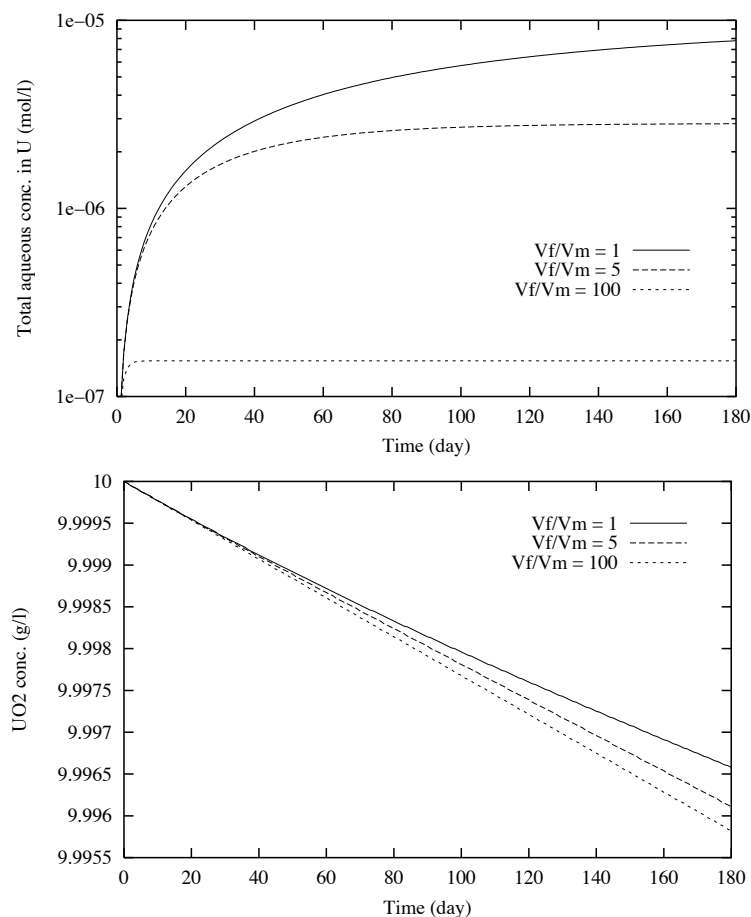
flush-with mobile-fraction {
    volume = 0.5 l
    pH = 6
    Eh = -0.2
    tot Na[+] = 5 mmol/l
    tot ClO4[-] = 5 mmol/l
}

samples = 180
select time in days
select UO2(am) in g/l
select aqueous{UO2[2+]}
```

The experiment takes 180 days. Note that the duration of the reaction path is set by the keyword `time` and is linearly sliced in *samples* steps<sup>1</sup>. The flush rate depends on the

---

<sup>1</sup>If the mass of a solid under kinetic constraints decreases of more than 50 % during an elementary time step, CHESS automatically reduced the step as far as necessary.



**Figure 6.6:** Global dissolution rate of  $\text{UO}_2(\text{am})$  for different flush rates.  $V_f$  and  $V_m$  stand respectively for the volume of the flushing solution and the volume of the mother solution.

duration of the experiment and on the ratio between the volume of the flushing solution and the volume of the mother solution. The global dissolution rate of  $\text{UO}_2(\text{am})$  is a function of the kinetic of dissolution itself *and* the flush rate as shown in Figure 6.6. Much more information can be obtained from this kind of simulations. It shows how a initially *static* simulation model can be used to approach modelling of dynamic systems. Nevertheless, much more precise modelling of geochemical systems is often required, hence the need for coupled hydrodynamic/geochemical tools.

## A Units

In the input scripts or the databases related to CHESS, most of the keywords refers to variables or parameters which are not dimensionless but require units. The units are seldomly constrained in CHESS, and the user can specify its own choice (for instance mg/l instead of mol/l). If no unit is provided for, default values will be assumed which are always SI units *except* for the temperature which uses °C by default. We strongly recommend to specify units in order to avoid confusion and maintain readability of input files.

Table A.1 displays the units recognized by CHESS and their default values. Most units can be preceded with **k** (kilo, times  $10^3$ ), **m** (mili, times  $10^{-3}$ ), **u** (micro, times  $10^{-6}$ ), **n** (nano, times  $10^{-9}$ ) and **p** (pico, times  $10^{-12}$ ).

Entity	Default	Alternatives
charge	C	mC, uC, ...
energy	J	kJ ...
length	m	dm, cm, um, ...
mass	mol	mmol, umol, ... but also kg, g, mg, ...
potential	V	mV, uV, ...
surface	m2	um2, nm2, ...
temperature	C	K
time	sec	min, hour, day, year
volume	m3	l, ml dm3, cm3, ...

**Table A.1:** Units by default and their alternatives recognized by CHESS.

Concentration is defined as [mass]/[volume], specific surface area as [surface]/[mass], volumic surface area as [surface]/[volume], surface charge as [charge]/[surface] and site density or exchange capacity in terms of [mass]/[surface]. The kinetic parameters Arrhenius energy and rate are respectively defined in terms of [J/mol] (fixed value) and [mass]/[surface]/[time]



Acetic_acid(aq)	Acetone(aq)	Benzene(aq)	Butanoic_acid(aq)
Ethanamine(aq)	Ethane(aq)	Ethanol(aq)	Ethylene(aq)
Formic_acid(aq)	Glycolic_acid(aq)	Glycine(aq)	Lactic_acid(aq)
Malonic_acid(aq)	Methane(aq)	Oxalic_acid(aq)	Pentanoic_acid(aq)
Propanoic_acid(aq)	Succinic_acid(aq)	Toluene(aq)	oPhthalate[-]

**Table B.1:** Organic species present in the full LLNL EQ3/6 database, but not included in the moderated CHESS database.

## B Thermodynamic databases

### B.1 Available databases

Initially, CHESS was provided as a solver only without any database. Accordingly, the responsibility of which database should be used was left to the geochemical competence of the user. However, this appeared to be a major handicap for novice users, who had to learn not only how to run CHESS but also how to format a database. It was then decided to provide a CHESS database based on the LLNL (EQ3/6) database but enriched in sorption sites and colloidal species, and several public available databases to the CHESS users group. The different databases have been rewritten in a specific CHESS *format* which is structured, compact and keyword-based. They are all available via the World Wide Web at <http://chess.enscm.fr>.

The databases available for CHESS version 2.4 are:

- **The CHESS database “chess.tdb”** is a CHESS-formatted version of EQ3/6 (V.8-R.6) database (Wolery (1992)), moderated by disregarding a number of organic redox-species and their derived species (see Table B.1), but extended with colloids and sorption sites. This database contains 1251 aqueous species including 98 redox couples, 1121 minerals, 91 gases, 74 sites, 3 inorganic colloids, and 3 organic colloids.
- **The LLNL database “eq36.tdb”** is a CHESS-formatted version of the full EQ3/6 (V.8-R.6) database (Wolery (1992)).
- **The CHEMVAL database “chemval4.tdb”** is CHESS-formatted version of the CHEMVAL database V.4 developed in the framework of an European inter-comparison exercise (Read and Falck (1996)).
- **the NEA database “nea.tdb”** is a CHESS-formatted version from the NEA thermochemical database project TDB (see <http://www.oecdnea.org>).

Without any specific needs, the use of **chess.tdb** is recommended. Most of the sorption data have been taken from Dzombak and Morel (1990), but new data (mainly involving colloids) have been added as well. Their references can be found into the database files themselves.

H2O	Ag[+]	Al[3+]	Am[3+]	Ar(aq)
Au[+]	B(OH)3(aq)	Ba[2+]	Be[2+]	Br[-]
Cd[2+]	Ca[2+]	Ce[3+]	Cl[-]	Co[2+]
CrO4[2-]	Cs[+]	Cu[2+]	Dy[3+]	Er[3+]
Eu[3+]	F[-]	Fe[2+]	Ga[3+]	Gd[3+]
H[+]	H2AsO4[-]	HCO3[-]	HP04[2-]	He(aq)
Hf[4+]	Hg[2+]	Ho[3+]	I[-]	In[3+]
K[+]	Kr(aq)	La[3+]	Li[+]	Lu[3+]
Mg[2+]	Mn[2+]	MoO4[2-]	NH3(aq)	Na[+]
Nd[3+]	Ne(aq)	Ni[2+]	Np[4+]	O2(aq)
Pb[2+]	Pd[2+]	Pr[3+]	Pu[4+]	Ra[2+]
Rn(aq)	Rb[+]	ReO4[-]	RuO4[2-]	SO4[2-]
Sb(OH)3(aq)	Sc[3+]	SeO3[2-]	SiO2(aq)	Sm[3+]
Sn[2+]	Sr[2+]	Tb[3+]	TcO4[-]	Th[4+]
Ti(OH)4(aq)	Tl[+]	Tm[3+]	UO2[2+]	VO[2+]
WO4[2-]	Xe(aq)	Y[3+]	Yb[3+]	Zn[2+]
Zr(OH)2[2+]	O2(aq)			

**Table B.2:** List of the basis species of the full CHESS database version 2.4.

The set of default basis species are conventionally the building blocks of all the secondary species of the database. Table B.2 lists the default basis species of the full CHESS database. Note that they are all aqueous, which is an arbitrary choice. It is not necessary to select the principal components from the default set of basis species, because CHESS knows how to implicitly swap species from the derived field to the basis (i.e. *species promotion*)<sup>1</sup>. This is how minerals, colloids and gases are included in the system. Very often, it is even illogical to select default basis species. Think, for instance, to  $\text{Fe}^{2+}$  (written as **Fe[2+]** in CHESS format) in a highly oxidizing environment ... The model will use valuable time to find out that it is more likely to use hematite or another hydrous ferric oxide instead, something which can be anticipated by the user. A choice of principal components driven by chemical tuition is sometimes even necessary in order to achieve convergence, especially in redox systems.

As discussed in Chapter 3, the natural waters are commonly in disequilibrium with respect to some or many of the redox species. In such situations, the command **redox = disabled of ...** can be used to prevent some specific species representing different oxidation states of an element to be link by equilibrium reactions. Once a redox coupled has been disabled, CHESS considers the disabled species as equivalent to a basis species. The disabled species has thus its own mass balance and independent entry in the input script. The coupled redox species are listed Table B.3 in the case of the CHESS reduced database.

---

<sup>1</sup>There is one exception: you must specify a default basis species if you are using aqueous-concentration!



## B.2 The CHESS database format

CHESS uses a specific, keyword based database format. The keyword-based approach of formatting the database has a number of important advantages. First, the database is more compact (about one third of the size of the original LLNL version), hence its reading is much faster. Second, the format is evolutive, i.e. new attributes can be added without losing “downward compatibility” with previous databases. The format guarantees an optimal readability and the keywords are intuitive, hence easy to remember. Updating the database with new data is therefore straightforward even for novice modelers. And last but not least, the keyword based approach allows for conversion to other formats for other models.

The data is compiled in ASCII format in a file of over 15,500 lines (about 550 Kb). The file starts with comments to identify the origin and version of the database and a series of general constants. The CHESS database is then structured according to major fields. A field is a specific area delimited by brackets. Everything within brackets belongs to its specifier, which is the name of the field. The following major fields are present: **basis-species**, **redox-couples**, **aqueous-species**, **gaseous-species**, **minerals**, **colloids**, **organic-matter** and **surface-sites**.

Each major field consists of a number of minor fields, which are species with the type of the major field. For example, the field **aqueous-species** contains the species **Al(OH)<sub>2</sub>[+]**. All attributes and characteristics of the species are given in its associated field:

```
Al(OH)2[+] {
  composition = -2 H[+], 1 Al[3+], 2 H2O
  logK = -12.1394(0), -10.5945(25), -8.7455(60), -6.9818(100)\
        -5.146(150), -3.5858(200), -2.2019(250), -0.9295(300)
  radius = 2e-09
}
```

A number of general formatting rules apply to the database. Each major field must be opened with “{” and closed with “}”. Comments are possible using the comment-specifier “#”. The order of the fields is not fixed, you may change it. But the actual order is optimized for reading by CHESS. Empty lines and white spaces at the start of each line are ignored. The special line-break character, “\”, extends reading to the next line. The logarithms of formation constants can be introduced for *arbitrary temperatures* (in °C) in the database. CHESS used this list to compute by interpolation the formation constant for any temperature between 0 and 300 °C. The log(*K*) list can be reduced up to one single element.

Here is a list of the minor field structure for each major field. The reader should refer to Appendix A for the default and alternative units recognized by CHESS.

### Basis-species

The following minor field

```
Ag[+] {
```



```

molew. = 107.868
radius = 1.25e-09
element = Ag
name = silver
}

```

provides for the basis species **Ag[+]**, respectively, its (atomic) molecular weight, a radius size (not used in CHESS alone), and its chemical symbol and name.

### Redox-couples

The following minor field

```

HS[-] {
  composition = -2 O2(aq), 1 H[+], 1 S04[2-]
  logK = -152.099(0), -138.317(25), -122.137(60), -107.03(100)\
        -91.7855(150), -79.4025(200), -69.0257(250), -60.0062(300)
  radius = 1.75e-09
}

```

provides, for the redox species **HS[-]**, its formation reaction in terms of the basis species, a list of related logK values at different temperatures in °C. Note that a radius may be given for each ion. The ion radius is not used in CHESS, but may be important for e.g. transport models in order to calculate the specific diffusion coefficient.

### Aqueous-species

The following minor field

```

MgHC03[+] {
  composition = 1 HC03[-], 1 Mg[2+]
  logK = 1.0798(0), 1.0357(25), 1.1638(60), 1.4355(100)\
        1.8804(150), 2.4146(200), 3.0493(250), 3.8424(300)
}

```

provides, for the aqueous species **MgHC03[+]**, its formation reaction in terms of the basis species, a list of related logK values at different temperatures in °C. An aqueous species is normally reported to the default basis species, with however the major exception of the species related to redox couples. In the example of **FeCl[2+]**,

```

FeCl[2+] {
  composition = 1 Cl[-], 1 Fe[3+]
  ...
}

```

the composition does not refer to **Fe[2+]**, but rather to **Fe[3+]** which shares the same oxidation state than **FeCl[2+]**. Wherever possible, this balance of the composition permits the redox decoupling option to operate.

## Gaseous-species

The following minor field

```

C02(g) {
  composition = -1 H2O, 1 H[+], 1 HC03[-]
  logK = 7.6765(0), 7.8136(25), 8.0527(60), 8.3574(100)\
        8.7692(150), 9.2165(200), 9.7202(250), 10.3393(300)
}

```

provides, for the gaseous species **C02(g)**, its formation reaction in terms of the basis species and a list of related logK values at different temperatures in °C.

## Minerals

```

Goethite {
  composition = -3 H[+], 1 Fe[3+], 2 H2O
  logK = -1.5252(0), -0.5345(25), 0.6(60), 1.6142(100)\
        2.6004(150), 3.399(200),
  vol.weight = 4267.71 kg/m3
}

```

provides, for the mineral species **Goethite**, its formation reaction in terms of the basis (or redox) species, the related logK values at different temperatures in °C, and its volumic weight. One or several sorption sites can be directly defined in the mineral minor field. For instance, in the case of a clay mineral with ion exchange abilities, the field

```

Illite {
  composition = -8 H[+], 0.25 Mg[2+], 0.6 K[+], 2.3 Al[3+], 3.5
  SiO2(aq), 5 H2O
  logK = -11.3859(0), -9.026(25), -5.555(60), -2.0472(100)\
        1.6128(150), 4.6923(200), 7.4468(250), 10.0976(300)
  vol.weight = 3000 kg/m3
  site Illite(Na) {
    content = 1 Na[+]
    exch.cap. = 4.5 umol/m2
  }
}

```

introduces the site **Illite(Na)** which becomes a new basis species attached to the clay. The keyword **content** specifies the species which are susceptible to be released from the site, **Na[+]** in the example. The exchange capacity (or site density) is expressed in  $\mu\text{mol}/\text{m}^2$ . The number of exchange sites actually available in a system is calculated in function of the specific (or volumic) surface area given in the input script and the amount of mineral in the system. In some specific cases the composition can be ignored (or set to **unknown**) and  $\log(K)$  skipped.

## Colloids

The following minor field

```

>HF0 {
  composition = 3 H2O   -3 H[+]   1 Fe[3+]
  logK = -2.1377
  vol.weight = 3113.9   kg/m3
  radius = 10 nm
  site >HF0(s)-OH {
    exch.cap. = 0.093 umol/m2
  }
  site >HF0(w)-OH {
    exch.cap. = 3.745 umol/m2
  }
}

```

provides first, for the colloidal species >HF0, its formation reaction in terms of the basis species, and a list of related logK values at different temperatures in °C, and its volumic weight. Colloids are particles of small sizes, hence of large specific surface areas. The radius size or the specific surface area is therefore a main characteristic of colloids, which has to be associated with the species. In our example, the model will assume that >HF0 is a spherical particle with a radius of 50 nm and calculates the specific surface area (using  $As = 3/(\rho a)$ ), where  $\rho$  is the volumic weight and  $a$  the radius of the particle. If, however, the colloid is not spherical (e.g. a clay mineral), it becomes more insidious to provide directly the specific surface area instead of the radius. The species >HF0 may equivalently be entered like this:

```

>HF0 {
  ...
  vol.weight = 4267.71 kg/m3
  surface = 14.06 m2/g
  ...
}

```

One or several sorption sites can be directly defined in the colloid minor field. In this example, two types of sorption sites (functional groups) are introduced in the second part of the field: a strong site denoted by HF0(s)-OH and a weak site represented by >HF0(w)-OH. Each site is a new basis species *attached* to its mother-species. The number of exchange sites actually available in a system is calculated in function of the specific surface area and the total amount of colloids. Note that for a site such as HF0(w)-OH, the keyword **content** may be omitted since H[+] which is always present in solution is the only released species.

An interesting new feature of CHESS is the ability to introduce not one colloid size, but merely a size *distribution*. This is introduced by a series of

- the frequency (obtained by SEM counting, for example)
- the radius

Here is an example of colloidal amorphous silica with a size distribution :

```

>Silica {
  vol.weight = 4826.55 kg/m3

```

```

radius {
  0.043 x 30.25 nm
  0.157 x 33.75 nm
  0.228 x 37.60 nm
  0.166 x 41.85 nm
  0.084 x 46.65 nm
  0.080 x 51.95 nm
  0.089 x 57.90 nm
  0.063 x 64.50 nm
  0.037 x 71.85 nm
  0.028 x 80.05 nm
  0.019 x 89.20 nm
  0.006 x 99.35 nm
}
site >Silica-OH {
  exch.cap. = 12 umol/m2
}

```

Note that the composition is omitted: a size distribution is not possible in combination with a known composition (i.e., the colloids may not dissolve).

### **organic-matter**

The **organic-matter** minor fields are, for the moment, identical to the inorganic colloids. For example:

```

>AHA {
  composition = unknown
  vol.wt. = 1200 kg/m3
  radius = 5 nm
  site >AHA(1)-COOH {
    exch.cap. = 6 umol/m2
    molew. = 45.01
  }
  site >AHA(2)-COOH {
    exch.cap. = 3 umol/m2
    molew. = 45.01
  }
  site >AHA-OH {
    exch.cap. = 1.6 umol/m2
    molew. = 17.0073
  }
}

```

stands for an Aldrich humic acid with three different types of sites. Note that the elemental composition of an humic acid is rarely known in general. Note that a organics (and solid species in general) may contain as many sites as desired: it offers henceforth a (not very elegant) possibility to ‘emulate’ the continuous site-distribution model.

**Surface-sites**

The following minor field

```
>HF0(s)-0Zn[+] {  
  composition = 1 >HF0(s)-OH  -1 H[+]  1 Zn[2+]  
  logK = 0.99  
}
```

provides, for the site species `>HF0(s)-0Zn[+]`, its formation reaction in terms of the basis species (aqueous and site), and in this example, a single  $\log(K)$  value.



## C Keywords glossary

### C.1 Introduction

The entire set of the CHESS keywords is presented below. The synopsis of each keyword is fully detailed, its functionality is summarized and illustrated by some short examples. The term *species* denotes any aqueous, colloidal, gaseous, mineral or organics species. When relevant, the possible choices are separated by the symbol | and the options are given between brackets.

The keyword and its arguments are separated by one or more spaces, a comma, a “tab” or a combination of these characters. All keywords can be abbreviated, provided there is no confusion possible with other ones.

Some keywords are only valid within the scope of another keyword. For example, keyword **rate** can only be used within the scope of keyword **kinetics**. For each keyword, the scope is specified. Note that GLOBAL means that the keyword may appear anywhere, and SHELL indicates that the keyword is valid in interactive mode only.

**activity** LOCAL/GLOBAL

*syntax* : activity *species* = *value*

*description* : constrains the activity of (generally) an aqueous species. The activity remains fixed for the equilibrium calculations, unless specified otherwise by keyword **free**.

*See also* : colloid, concentration, Eh, fugacity, mineral, pe, pH, total-concentration.

*examples* : `activity HC03[-] = 0.001`  
`act U02(C03)3[4-] = 1e-6`

---

**aqueous-concentration** LOCAL/GLOBAL

*syntax* : aqueous-concentration *species* = *value* [*unit*]

*description* : sets the total aqueous concentration of a species. A unit may be provided, otherwise mol/m<sup>3</sup> (mmol/l) is assumed. The aqueous concentration is the total concentration minus the sum of the mineral phases of this component. This keyword can be used for basis species only.

*See also* : activity, concentration.

*examples* : `aqueous S04[2-] = 500 mg/l`  
`aqueous Ba[2+] = 10 umol/l`

---

**arrhenius-energy** KINETICS

*syntax* : arrhenius-energy = *value unit*

*description* : sets the apparent activation energy of Arrhenius (in J/mol) for a kinetic reaction. The temperature dependency is introduced simultaneously through this keyword and the specification of the temperature (in Celsius) at which the rate constant is valid. This keyword is optional in the **kinetics** field.

*See also* : kinetics

*examples* : `kinetic of Calcite {`  
`rate(25) = 0.005 mol/m2/s`  
`arrhenius-energy = 5e4 J/mol`  
`}`



---

**balance**

LOCAL/GLOBAL

*syntax* : balance on *species*

*description* : designs the species to be used to adjust the electrical charge balance. The specified species must have a non-zero charge and constrained by its total concentration. The balancing feature is disabled by default.

*examples* : balance on Na[+]

---

**bring**

GLOBAL

*syntax* : bring *species* | *item* to *value* [*unit*] [, log]

*description* : the keyword **bring** sets a titration-like reaction path bringing the variable from its initial value to a given final value. A unit may be specified, otherwise mol/m<sup>3</sup> (mmol/l) is assumed. Linear steps from the initial state to the final state are considered by default, unless specified by the optional argument **logarithmic-steps** which enables logarithmic steps. Note that logarithmic steps are not allowed for some bring-reactions. More than one **bring** command may be introduced for the same system, provided that they are introduced on separate lines. Bring cannot be used with other reaction paths, such as flushing or mixing.

*examples* : bring pH to 12  
bring Eh to -230 mV  
bring temperature to 300 C  
bring UO2[2+] to 1 mmol/l, log  
bring Hematite to 10 g/l  
bring time to 10 years  
bring radius of >Quartz to 200 nm  
bring Fe to 99 mg/l

---

**cls**

SHELL

*syntax* : cls

*description* : clears the screen in interactive mode.

---

**colloid**

LOCAL/GLOBAL

**syntax** : `colloid species = value [unit] [, surface = value [unit]]`

**description** : sets the total concentration of a specified colloid. A unit may be introduced, otherwise mol/m<sup>3</sup> (mmol/l) is assumed. The default value for the specific surface is taken from the database, unless specified by the optional keyword **surface**. A unit may be provided such as m<sup>2</sup>/g, m<sup>2</sup>/mol or m<sup>2</sup>/l ([surface]/[mass] or [surface]/[water-volume] in general).

**examples** : `colloid >Quartz = 10 mg/l`  
`colloid >Hematite = 0.1 g/l, surface = 200 m2/g`

**see also** : mineral, organic, surface, total-concentration.

---

**concentration**

LOCAL/GLOBAL

**syntax** : `concentration species = value [unit]`

**description** : sets the free concentration of an aqueous species, colloid or mineral. The concentration remains fixed for the equilibrium calculations unless specified otherwise by keyword **free**. The total-concentration is adjusted in order to maintain the concentration fixed. A unit may be provided, otherwise mol/m<sup>3</sup> (mmol/l) is assumed.

**examples** : `concentration Cd[2+] = 10 umol/l`  
`conc Quartz = 50 g/l`

**see also** : activity, colloid, free, fugacity, mineral, total-concentration

---

**correction-model**

GLOBAL

**syntax** : `correction-model = model-type`

**description** : sets the function used for activity corrections. CHESS presently recognizes four different types of models, i.e. *davies*, *truncated-davies*, *debye-huckel* and *b-dot*. The option by default is *truncated-davies*.

**examples** : `correction = b-dot`

---

**database-filename**

GLOBAL

*syntax* : database-filename = *filename*

*description* : sets the path and name of the file which contains the thermodynamic data. The default value is system dependent, but usually **c:\chess\tdb\chess.tdb** for MS-Windows and **/usr/local/chess/tdb/chess.tdb** for Unix systems.

*examples* : **database = organics.tdb**

---

**dissolution**

GLOBAL

*syntax* : dissolution = **disabled** | **enabled** [ of *species* [, *species* ... ] ]

*description* : disables the dissolution of solids in general. If the dissolution is disabled, the entire process of dissolution of all colloidal or mineral species which are introduced by the user in the input script is prevented. However, it is also possible to "fine-tune" the model behaviour by disabling dissolution of one or several solids specifically. Dissolution is enabled by default.

*examples* : **dissolution = disabled**  
**dissolution = disabled of >Quartz, Quartz**

*see also* : colloid, mineral, precipitation

---

**Eh**

LOCAL/GLOBAL

*syntax* : Eh = *value* [*unit*]

*description* : constrains the redox potential of the solution. The redox potential remains fixed for the equilibrium calculations, unless specified later on by the keyword **free**. A unit may be provided, otherwise Volts (V) is assumed. The keyword **Eh** automatically triggers the redox, i.e., as if **redox = enabled** had been set.

*examples* : **Eh = -100 mV**

*see also* : free, redox, pe

---

**electrostatics**

GLOBAL

*syntax* : `electrostatics = enabled | disabled`

*description* : disables the electrostatic correction term used in surface complexation modelling. The model behaves so according to the free ligand complexation approach. Electrostatic correction is automatically enabled by CHESS, using the double layer theory.

*examples* : `electrostatics = disabled`

---

**exclude**

GLOBAL

*syntax* : `exclude species | [, species [, species ... ]]`

*description* : excludes one or more species or sites from the system, as if they were not present in the database. Several **exclude** command can be introduced in the input script, but one may also exclude *groups* of species, such as colloids, organics, gases, minerals, organics and sites.

*examples* : `exclude UO2(OH)2(aq), Hematite`  
`exclude colloids, sites`  
`exclude >HFO(w)-OCa[+]`

*see also* : include

---

**flush-with**

GLOBAL

*syntax* : `flush-with [mobile-fraction] {`  
    ...  
}

*description* : sets a reaction path for flushing the initial solution with a second solution which is specified in the scope of the **flush-with** field. By default the volume of the second solution is 1 liter, which may be modified by keyword **volume**. For each sample (the number of samples is 100, unless specified otherwise by keyword **samples**), a fraction or the total volume of the mother solution is replaced by the flush-with solution. This fraction is defined by the ratio of the volumes of both solutions. The option **mobile-fraction** is useful if the secondary solution contains mineral phases.

*examples* : flush-with {  
    pH = 5  
    tot Cl[-] = 1 mmol/l  
    tot Na[+] = 1 mmol/l  
    balance on Cl[-]  
}

*see also* : bring, mix-with, samples, volume

---

## free

GLOBAL

*syntax* : **free** *species* [, *species* [, *species* ... ]] [, **early**]

*description* : sets one or more species free for variation after the initial equilibrium calculation. The keyword takes an optional flag, **early**, which allows to liberate the species *before* precipitation or dissolution of solid phases.

*examples* : **free** pH

*see also* : pH, Eh, pe

---

## fugacity

LOCAL/GLOBAL

*syntax* : fugacity *species* = *value*

*description* : constrains the fugacity of a gas. The fugacity remains fixed for the equilibrium calculations, unless specified later on by the keyword **free**.

*examples* : **fugactiy** CO2(g) = 5e-4  
            **fug** O2(g) = 0.1

*see also* : activity, concentration, free

---

## help

SHELL

*syntax* : **help** [*keyword*]

*description* : provides on-line help in interactive mode. Typing **help** gives a short introduction of how to start working with CHESS. Typing **help keyword** displays some help and one or more examples of application of the selected keyword.

*examples* : `help`  
           `help flush`

---

## **include**

GLOBAL

*syntax* : `include species [, species [, species ... ]]`

*description* : includes one or more species or sites in the system. This keyword is generally used in combination with **exclude**, e.g., excluding minerals but including two or three minerals of interest for your system.

*examples* : `include UO2F[+], UO2F2(aq), UO2F3[-]`  
           `exclude minerals, colloids`  
           `include Dewindtite`

---

## **interface-model**

GLOBAL

*syntax* : `interface-model = model`

*description* : sets the type of interface model used for solid-solution interactions. By default, the model uses the common mass-law equations for calculating surface complexation and cation exchange. However, an alternative approach is available which uses a mass action law amended for surface reactions. The actual choices are therefore **surface-complexation** (the option by default) or **amended-surface-complexation**. See van der Lee (1998) for details.

*examples* : `interface-model = amended`

*see also* : `Kd`

---

## **Kd**

GLOBAL

*syntax* : `Kd of species = value`

*description* : enables a Kd-reaction to occur for a given aqueous species and sets the Kd-value. This value is dimensionless, i.e. the common unit for Kd ( $\text{m}^3/\text{kg}$ ) multiplied with the total solid concentration ( $\text{kg}/\text{m}^3$ ). You can trace the amount of fixed solute with the `fixed{solute}` definition in the **select** command.

*examples* : Kd of Pb[2+] = 20  
               select aqueous{Pb[2+]}, fixed{Pb[2+]}

*see also* : interface-model, select

---

## kinetics

GLOBAL

*syntax* : kinetics of *species* {  
               ...  
               }

*description* : defines (and enables) the kinetic parameters of dissolution and precipitation reactions of a solid. The field includes the compulsory keywords **rate** and several optional keywords, such as **arrhenius-energy**, **power** and **oversaturation-index**. Note that the concentration and specific surface of the reacting solid must be defined in the input file with a keyword such as **colloid**, **concentration** or **mineral**.

*examples* : kinetics of Calcite {  
               rate = 7e-4 mol/cm2/s  
               power of H[+] = 1  
               }

*see also* : arrhenius-energy, rate, power, oversaturation-index, time

---

## logK

GLOBAL

*syntax* : logK of *species* = *value* | *polynome*

*description* : sets a new value of the logarithm of the formation constant of *species*. Eventually, an entire new polynome of log-K values may be introduced using a format identical to the database. The temperature values must be given in degree Celsius. In both cases, the new definition overwrites the database definition.

*examples* : logK of >Quartz-0Zn[+] = 0.5  
               logK of ZnOH[+] = -9.812(10), -8.032(20), -7.835(50),\  
                                   -7.601(75), -7.41(100), -6.9(150)

---

## maxiterations

GLOBAL

*syntax* : maxiterations of *procedure* = *value*

*description* : sets the maximum number of iterations of the different iterative procedures of the model, i.e., the Newton-Raphson procedure (1000 by default) the procedure for finding a stable assemblage of solids (100 by default).

*examples* :   maxit of newton-raphson = 500  
                  maxit of solids = 150

*see also* : precision

---

## mineral

LOCAL/ GLOBAL

*syntax* : mineral *species* = *value* [*unit*] [, surface = *value* [*unit*]]

*description* : sets the total concentration of a specified mineral. A unit may be provided, otherwise mol/m<sup>3</sup> (mmol/l) is assumed. The default value for the specific surface is based on the assumption of a spherical shape of the mineral. The keyword **surface** sets the specific surface in units such as m<sup>2</sup>/g, m<sup>2</sup>/mol or m<sup>2</sup>/l ([surface]/[mass] or [surface]/[water-volume] in general).

*examples* :   mineral Diaspore = 10 mg/l  
                  mineral Hematite = 0.1 g/l, surface = 200 m2/g

*see also* : colloid, organic, total-concentration.

*remark* : specifying a volumic surface (e.g. in m<sup>2</sup>/l) disables the correction of the available surface for kinetics or adsorption reactions as the mineral grows or dissolves. Otherwise, the actual available surface is recalculated when the mass of the mineral evolves.

---

## mix-with

GLOBAL

*syntax* : mix-with [mobile-fraction] {  
                  ...  
                  }

*description* : sets a reaction path for mixing an initial system with a second one specified in the scope of the *mix-with* field. By default the volume of the second solution is one liter, but may be modified by keyword **volume**. Mixing takes 100 linear steps, unless specified otherwise by the keyword **samples**). At the end of the reaction path, the solution is a perfect mix of the two solutions. The option **mobile-fraction** can be used if the mix-with solution contains minerals which should not be mixed with the mother solution.



```
examples : mix-with {  
           pH = 8  
           tot Ca[2+] = 200 mg/l  
           tot HCO3[-] = 13 mg/l  
           tot Zn[2+] = 50 ug/l  
         }
```

see also : bring, flush-with, samples

---

## organic

LOCAL/GLOBAL

syntax : organic *species* = *value* [*unit*] [, surface = *value unit*]

*description* : sets the total concentration of a specified colloid or coating of organic matter. A unit may be introduced, otherwise mol/<sup>3</sup> (mmol/l) is assumed. The default value for the specific surface is taken from the database, unless specified by the optional keyword **surface**. A unit may be provided such as m<sup>2</sup>/g, m<sup>2</sup>/mol or m<sup>2</sup>/l ([surface]/[mass] or [surface]/[water-volume] in general).

examples : organic >AHA = 5 mg/l

see also : colloid, mineral, surface, total-concentration

---

## output-filename

GLOBAL

syntax : output-filename = *filename*

*description* : sets the path and name of the file which contains the results of a single equilibrium calculation, or the results of the initial and final states of a reaction path. The file by default is **CHESS.out** in the current work-directory.

examples : output-filename = ../res/myresults.out  
 output = Zn\_results.out

see also : database-filename, path-filename

---

## oversaturation-index

KINETICS

syntax : oversaturation-index = *value*

*description* : sets the oversaturation index for the solid for which this kinetic field is used. No precipitation occurs before this limit is reached. The value should be greater than 0.

*examples* : `oversaturation-index = 2.5`

*see also* : kinetics

---

## path-filename

GLOBAL

*syntax* : `path-filename = filename`

*description* : sets the path and name of the file which contains columns of output corresponding to the items specified with the keyword **select** during a reaction path calculation. The file by default is **CHESS.res** in the current work-directory.

*examples* : `path-filename = ../res/myresults.res`  
`path = Zn_results.res`

*see also* : database-filename, output-filename

---

## pe

LOCAL/GLOBAL

*syntax* : `pe = value`

*description* : sets the *pe* of the solution which will remain fixed for the equilibrium calculations, unless specified otherwise by keyword **free**. Setting the *pe* automatically triggers the redox (*redox = enabled*).

*examples* : `pe = 9`

*see also* : Eh, free, redox

---

## pH

LOCAL/GLOBAL

*syntax* : `pH = value`

*description* : sets the pH of the solution. The pH remains fixed for the equilibrium calculations, unless specified otherwise by keyword **free**.

*examples* : `pH = 10`

*see also* : activity, free

---

## **power** KINETICS

*syntax* : power of *species* = *value* [, at *value* C]

*description* : allows to take into account the catalyzing or inhibiting effect of one or several aqueous species through the product of their activities brought to user-provided powers. The keyword also sets the power of “omega”, e.g. the hypothetical solid activity. Only one **power** declaration per line is possible. This keyword is optional in the **kinetics** field.

*examples* : 

```
kinetics of Calcite {  
    rate = 7e-4 mol/cm2/s  
    power of H[+] = 1  
    power of omega = 1.5  
}
```

*see also* : kinetics, arrhenius-energy, power, rate, time, oversaturation-index

---

## **precipitation** GLOBAL

*syntax* : precipitation = **disabled** | **enabled** [ of *species* [, *species* ... ]]

*description* : used to disable the precipitation of colloids and minerals. With a command like **precip = disabled**, the entire process of precipitation of all colloidal or mineral species is disabled. However, it is also possible to “fine-tune” the model behaviour by disabling precipitation of one or several solids specifically. By default, **precipitation** is enabled.

*examples* : 

```
precipitation = disabled  
precipitation = disabled of Calcite, >HF0
```

*see also* : dissolution

---

## **precision** GLOBAL

*syntax* : precision of *procedure* = *value*

*description* : sets the precision of several iterative procedures of the model, such as the Newton-Raphson procedure (**newton-raphson**), the precision in adjusting the total concentration of the species used for charge balancing (**electroneutrality**), or the precision of the coupling procedure (**coupling**, HYTEC only).

*examples* : **precision of newton-raphson = 1e-6**

*see also* : maxiterations

---

**quit** SHELL

*syntax* : **quit**

*description* : terminates the CHESS interactive mode.

---

**rate** KINETICS

*syntax* : **rate = value [unit]**

*description* : sets the rate constant of a kinetic reaction in any units of the type [mass]/[surface]/[time] (mol/m<sup>2</sup>/s by default). This keyword is compulsory in the **kinetics** field. When the temperature dependency on the rate constant is introduced with the **Arrhenius-energy** keyword, one should specify the temperature at which a reference rate constant is valid.

*examples* : **rate = 9.9e-10 mol/cm<sup>2</sup>/s at 25 C**

*see also* : arrhenius-energy, kinetics, power, rate, time

---

**redox** GLOBAL

*syntax* : **redox = enabled ! disabled [of species[, species ... ]]**

*description* : used to trigger the redox process, or to decouple one or several redox species. Redox is disabled by default except if **Eh** or **pe** are specified.

*examples* : **redox = enabled**  
**redox = disabled of MnO<sub>4</sub>[-]**

*see also* : Eh, pe

---

**report**

GLOBAL

*syntaxe* : `report = full`  
          `report SI downto  $n$`   
          `report concentrations downto  $n$  [unit]`  
          `report sample value`

*description* : modifies the depth of details given in the general output file. The report may be set to *full* for a maximum of details, or the cut-off limits of species concentrations and saturation indices (*SI*) of solids may be specifically fixed. Report also takes the argument **sample** followed with a sample number. This will provide the outputfile with the detailed chemistry of the specific sample. Using **\*** instead of a sample number prints a report for all the samples.

*examples* : `report conc downto 1e-15`  
          `report SI downto -10`  
          `report = full`  
          `report sample 43`

*see also* : samples, output-filename

---

**samples**

GLOBAL

*syntax* : `samples = value`

*description* : sets the number of samples which will be taken during the calculation of a reaction path, such as **bring**, **flush-with** or **mix-with**. The default value is 100.

*examples* : `samples = 20`

---

**save**

SHELL

*syntax* : `save filename`

*description* : saves the script to file *filename* in interactive mode only.

*examples* : `save sorption-Pb.chs`

**select**

GLOBAL

**syntax** : select *item* [, *item* [, ... ]] [in *unit*]

**description** : specifies the items to be printed during a reaction path calculation. For each sample, the selected items are written to the path-file (see **path-filename**). The term *item* usually stands for the concentration of a species. A unit may be provided, otherwise the default unit of the selected item is assumed. A wide range of general items or special keywords may be selected:

1. General items:
  - **balance**
  - **Eh** [in *unit*] (in V by default)
  - **ionic-strength**
  - **pe**
  - **pH**
  - **samples**
  - **saturation-indices**
  - **temperature** [in *unit*] (in °C by default)
  - **time** [in *unit*]
  - **volume** [in *unit*]
2. Basis species (*species* is a basis species only), in mmol/l unless specified otherwise:
  - **all**{*species*} for the total concentration of *species*
  - **aqueous**{*species*} for aqueous fraction of the total concentration of *species*
  - **colloid**{*species*} for colloidal fraction of the total concentration of *species*
  - **fixed**{*species*} for fixed fraction of total concentration *species*
  - **gaseous**{*species*} for the gaseous fraction of the total concentration of *species*
  - **mineral**{*species*} for the mineral fraction of the total concentration of *species*
3. Colloids:
  - **radius**{*colloid*} for the radius of *colloid*.
4. Solids (colloids, organics or minerals):
  - **charge**{*solid*} for the surface charge of *solid* (in C/dm<sup>2</sup> by default)
  - **potential**{*solid*} for the surface potential of *solid* (in V by default)

- SI {*solid*} for the saturation index

See also `bring`, `flush-with`, `kinetics` and `mix-with`.

*examples* : `select pH, Ca[2+], F[-], Fluorite`  
`select Eh in mV`  
`select samples, aqueous{HC03[-]}, aqueous{Ca[2+]} in mg/l`  
`select fixed{Co[2+]} in umol/l`  
`select colloid{SiO2(aq)}, mineral{SiO2(aq)} in g/l`  
`select potential{Quartz} in mV`  
`select charge{>Hematite} in uC/cm2`  
`select saturation-indices`  
`select SI{Pyrite}, SI{Siderite}`  
`select *UO* in umol/l`

*remarks* : the unit specified for a `select` command concerns all items selected by that line. To set different units for different items, several lines of `select` must be introduced. The wild-character “\*” may be used to select all the species including a specific string of characters in their writing (such as `Zn*`, `*UO2*`, etc.).

---

## show

SHELL

*syntax* : `show [keywords]`

*description* : with no arguments, it shows the actual script in interactive mode only. Additionally, `show` may be used with *keywords* to show all the available keywords.

*examples* : `show keywords`

---

## temperature

LOCAL

*syntax* : `temperature = value [unit]`

*description* : sets the temperature of the solution. By default, the temperature is fixed at 25 °C. Note that the model assumes Celsius by default (the only exception on the SI unit standard).

*examples* : `temperature = 60 C`  
`temp = 293 K`

---

## time

GLOBAL

*syntax* : `time = value [unit]`

*description* : sets the total available time period for a flush or mixing reaction path with kinetic reactions. reach equilibrium. The keyword can also be used in conjunction with the **bring** command to set the time period of **kinetics** reaction paths.

*examples* : `time = 60 min`

*see also* : kinetics, bring

---

## **total-concentration**

LOCAL/GLOBAL

*syntax* : `total-concentration species = value [unit]`

*description* : sets the total concentration of a species. A unit may be provided, otherwise mol/m<sup>3</sup> (mmol/l) is assumed.

*examples* : `total-concentration Co[2+] = 1 mmol/l`  
`tot FeCO3[+] = 50 ug/l`  
`tot Pyrite = 10 mg/l`

*see also* : activity, colloid, fugacity, mineral

---

## **verbose**

GLOBAL

*syntax* : `verbose = enabled`

*description* : puts the model in verbose mode, i.e. it writes more details to the screen concerning the calculations.

---

## **volume**

LOCAL

*syntax* : `volume = value [unit]`

*description* : sets the volume of the initial solution and/or the subsystem solution for **flush-with** and **mix-with** reaction paths. By default, the model assumes one liter. A unit may be provided, otherwise m<sup>3</sup> is assumed.

*examples* : `volume = 250 ml`

*see also* : flush-with, mix-with

---



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