HYDROGEOCHEMICAL MODELING WITH PHREEQC

PHREEQC is used for simulating a variety of reactions and processes in natural waters or laboratory experiments. PHREEQC needs an input file in which the problem is specified via KEYWORDS and associated datablocks. The keywords are summarized here in *get-going* sheets. A full description of many alternatives for input and the mathematical backgrounds can be found in the manual of the program by Parkhurst and Appelo (1999).

PHREEQC was developed for calculating '*real world*' hydrogeochemistry and it does help to keep the connection with the physical situation palpable and concrete. Thus, we may start imagining a laboratory table with flasks with solutions, bottles with chemicals, minerals and exchangers, gascontainers, pipettes, a balance and a centrifuge with accessories, where we want to do some experiments. We use the following **KEYWORDS**:

SOLUTION *m-n* for the composition and quantity of solutions in flasks *m* to *n*. We can **USE** a specific solution, or **MIX** fractions of solutions in one flask.

Various reactants can be added to the flask:
EQUILIBRIUM_PHASES for a combination of minerals and/or gases which react reversibly to a prescribed equilibrium;
EXCHANGE for the capacity and composition of an exchanger;
SURFACE for the capacity and composition of surface complexers;
REACTION for stepwise adding or removing chemicals, minerals or water;
KINETICS for chemicals which react depending on time and composition of the solution;
GAS_PHASE for a combination of gases in a specified volume or at a given pressure;
SOLID_SOLUTIONS for adding solid solutions of minerals;
REACTION_TEMPERATURE for changing the temperature of the flask.

END is the signal for PHREEQC to calculate the composition of the solution and the reactants in what is termed a *simulation*. The compositions can be stored in computer memory with **SAVE** solution *no*, **SAVE** exchange *no*, etc., to be used later on in the same computer run (the same input file) with **MIX** or **USE** solution *no*, **USE** exchange *no*, etc., where *no* is a number or a range of numbers. The results can also be printed, punched in a spreadsheet file, or plotted in a graph.

For defining the output we use:
PRINT to limit printout to specific items and to suspend/resume print options;
SELECTED_OUTPUT to obtain results in spreadsheet type format;
USER_PRINT, **USER_PUNCH** and **USER_GRAPH** for defining tailor-made, specific output.

Flow and transport in the field and in laboratory columns can be modeled with keyword **TRANSPORT** for 1D dispersive/diffusive transport including mobile/immobile zones.
For 3D transport, the code PHAST can be used from the US Geological Survey website.

Lastly, the chemical reactions which led to a given water quality can be recovered using keyword **INVERSE_MODELING**.

Parkhurst, D.L. and Appelo, C.A.J., 1999. User's guide to PHREEQC (version 2). US Geol. Surv. Water Resour. Inv. Rep. 99-4259, 312p.

Getting started

The program PHREEQC, the manual and various example files can be downloaded via links in: **www.xs4all.nl/~appt**. Download Vincent Post's windows version and run psetup.exe to install the program and databases in c:\Program Files\phreeqc. Click on the PHREEQC icon to start. You'll be located in the input window.

Various options can be set, click Edit, Preferences (or ALT+e, e) and make your choices. The directories and the database file can be selected, click Calculations, Files (ALT+c, f)

To the right of the input window is a frame with PHREEQC keywords and BASIC statements. Click on + to expand the keywords, click again on + to expand keyword SOLUTION to see the identifiers (sub-keywords) temp, pH, pe, and more. Double clicking on a keyword or identifier will copy it to the input window.

Example files are in c:\Program Files\PHREEQC\Examples. Open U_GEX1, click Files, Open (ALT+f, o), U_GEX1. The file appears in the input window:

```
#           Graphs Ca vs F concentration in equilibrium with fluorite
#
SOLUTION 1                      # distilled water
END
EQUILIBRIUM_PHASES 1            # equilibrium with Fluorite, CaF2
 Fluorite
REACTION                       # Change Ca concentration for plot
 Ca(OH)2  1
 0.05 0.1 0.2 0.5 1 2 3 5 7 9 12 14 mmol
USE solution 1
USER_GRAPH                     # various chart definitions are omitted here
 10 graph_x tot("Ca")*1e3
 20 graph_y tot("F")*1e3
END
```

Run the file, click the calculator icon, or Calculations, Start (ALT+c, s).

Quickly, the progress window reports 'Done'. Press Enter, and you'll be transferred to the output tab. It contains a complete listing and many details of the calculated solution compositions.

Click the Database tab. The basic data for calculating a speciation model appear, listed under keywords. The first one is keyword **SOLUTION_MASTER_SPECIES** which defines the elements and, among other things, their formula weights.

Click the grid tab. It contains rows with the Ca and the F concentrations in equilibrium with fluorite as written by **USER_GRAPH**.

Click the Chart tab. It shows a plot of the F *vs* Ca concentration in equilibrium with fluorite.

SOLUTION

The aqueous concentrations in a solution are defined with **SOLUTION**. The symbols for the elements are listed in the first column of **SOLUTION_MASTER_SPECIES** in the database.

```
                                # Information following a # is  not read

SOLUTION 1    Speciate an analysis, calculate saturation indices
 temp  25.                      # temperature in degrees Celcius, default = 25 C
 pH  7.0                        # default pH = 7.
 pe  4.0                        # pe = -log(electron activity), default = 4.
 -units  mmol/kgw               # default units mmol/kg water
 Ca  3.0                        # total dissolved Ca
 Na  1.0
 Alkalinity 3.8                 # mmol charge / kgw
 S 1.0                          # total sulfur, mainly sulfate, S(6), at pe = 4
 N(5) 0.2                       # nitrogen in the form of nitrate, N(5)
 Cl 1.0
 water  1                       # kg water, default = 1 kg
 density  1                     # density, default = 1 kg/L
END


# Example 2. define range of solution no's, and use mg/L units
#
SOLUTION 2-4                    # solutions 2, 3 and 4
 -units mg/l
 Ca 40                          # mol. weights listed under SOLUTION_MASTER_SPECIES
 Alkalinity 122 as HCO3         # HCO3 is used for recalculating to mol charge
END


# Example 3. Adjust concentration or pH to charge balance
#
SOLUTION 4                      # default pH = 7, temp = 25, -units mmol/kgw
 Na   2.0
 Cl   1.3   charge              # adapt Cl to obtain charge balance
END


# Example 4. Adjust pe to equilibrium with atmospheric oxygen
#
SOLUTION 6                      # see EQUILIBRIUM_PHASES (sheet # 3) for more info
 pe 10.0 O2(g) -0.68            # add PHASES name, SI = -0.68. P_gas =  10^-0.68
END


# Example 5. Enter a suite of samples in spreadsheet format
# The data are tab delimited
#
SOLUTION_SPREAD
 -units mg/l
 -temp 11
Ca      Cl      S(6)    Temp    Alkalinity      pH      Li
                                mg/l as HCO3            ug/l
87.7    22.7    94.4    13      233.4           7.3
78.6    35.3    87.4    13.1    221.7           7.1     4
75.0    24.9    83.2            221.3           6.9
```

Note. The default temperature of 11°C will be given to the third sample.

Mineral Equilibration

A solution can be equilibrated with minerals assembled together in **EQUILIBRIUM_PHASES**, or the initial concentration of a component can be adapted when defining the **SOLUTION**.

```
# Example 1. Equilibrate water with calcite and CO2
#
SOLUTION 1                  # default pH = 7, pe = 4, temp = 25, units = mmol/kgw
 Ca  3.0
 Alkalinity  4.0
 S(6)  1.0
EQUILIBRIUM_PHASES 1
 Calcite  0.0  10.0     # Mineral from database, SI = 0.0, amount = 10 mol
 CO2(g)  -2.0           # SI = - 2.0 or [P_CO2] = 10^-2.0, amount = 10 mol
END


# Example 2. Equilibrate with Fluorite, adding gypsum.
#
SOLUTION 2
 F  1.5 mg/kgw          # drinking water limit for F = 1.5 mg/L
EQUILIBRIUM_PHASES 2
 Fluorite  0.0  Gypsum  # obtain SI = 0. by adding Ca from gypsum
END                     # note the high SO4 concentration in the output...


# Example 3. Equilibrate by changing an initial concentration
#
SOLUTION 3
 Ca  3.0 Calcite        # adapt Ca to equilibrium with calcite
 Alkalinity  4.0
 S(6)  1.0
 F  0.1 Fluorite -1.0   # adapt F to SI = -1.0 for fluorite
END
```

Notes

The mineral names must be spelled exactly as entered in the database under **PHASES** (you can copy the name after selection with CTRL+c, then paste with CTRL+v).

Gas equilibria. The gas pressure can be varied, setting *SI*. The *SI* is equal to log(gas pressure / 1 atm).

Example 4 illustrates the different effects of equilibrating by adjusting the initial concentration, and by the reversible dissolution reaction that is simulated with keyword **EQUILIBRIUM_PHASES**.

```
# Example 4. Adjust the CO2 gas pressure to 10^-2.5 = 0.00316 atm
#
SOLUTION 1
 pH  7.0
 C(4)  1.0   CO2(g) -2.5 # Only TIC is adapted, pH remains 7.0
END

SOLUTION 2
 pH  7.0
EQUILIBRIUM_PHASES 2       # pH changes when carbonic acid dissolves
 CO2(g)  -2.5  10.0
END
```

Solution 1 obtains a large electrical imbalance, while solution 2 remains electrically neutral.

PHREEQC Output

Using **PRINT**, you can modify the print to the output tab by setting output block identifiers true or false. These identifiers can be clicked and copied to the input tab after expanding keyword PRINT in the right window. The option -reset false is rather essential when doing transport simulations.

```
PRINT
 -reset false        # suspend all print output
 -totals true        # will print Solution composition, Description of solution
 -status true        # shows calculation progress
```

To write specific output in spreadsheet format ('punch' to a file), use **SELECTED_OUTPUT**. The selected information is written to the file after each simulation.

```
SELECTED_OUTPUT
 -file   stine1.csv           # name of output file. OBLIGATORY
 -totals Fe Fe(2) Hfo_w       # total conc. in mol/kgw, MASTER_SPECIES element name
 -molalities Fe+2 CaX2        # molalities of species
 -activities Fe+2 H+          # log activities of species
 -eq  Calcite                 # equilibrium_phases, note abbreviation -eq
```

Notes
Element names given under -totals should comply with the MASTER_SPECIES element names (first column in the databases).

Species names given under -mol and -act and mineral names must match the database names.

In transport calculations, -punch_cells and -punch_frequency can be used to further limit the punchout to the selected_output file.

USER_PUNCH, **USER_PRINT** and **USER_GRAPH**

The USER_ keywords give access to the BASIC compiler which is built in PHREEQC. You can punch out your own variables to the selected_output file with **USER_PUNCH**, print to the output file with **USER_PRINT**, and plot in PHREEQC for Windows with **USER_GRAPH**.

```
USER_PUNCH
 -headings mg_Na/l P_CO2              # column heading in file
 -start                              # start of BASIC lines
 10 punch tot("Na")*22.999e3
 20 punch 10^(SI("CO2(g)"))
 -end                                # end of BASIC lines
END


USER_GRAPH                           # plot F and pH vs Ca concentration
 -start
 10 graph_x tot("Ca")*1e3            # mmol/L
 20 graph_y tot("F")*1e3
 30 graph_sy -la("H+")               # pH on secondary y-axis
 -end
END
```

The BASIC lines can be seen as spreadsheet formulas, with special functions which give access to the aqueous model. These functions are explained under keyword **RATES** in the PHREEQC manual, and listed in the PHREEQC BASIC statements at the right of the input window.

REACTION

The keyword **REACTION** is used to stepwise add reactants or amounts of minerals to the solution.

```
# Example 1. Add 5 and 10 mmol NaCl to 1 liter distilled water.
#
SOLUTION 1                          # Define start solution, just water
REACTION 1
 NaCl  1.1       # Reactant formula, stoichiometric coefficient in the reaction
 5e-3  10e-3                         # Add 1.1*5e-3 mol NaCl and 1.1*10e-3 mol NaCl
# 10e-3 moles in 2 steps        # alternate way of writing the steps
END


# Example 2. Add Calcite and CO2 to water
#
SOLUTION 2
REACTION 2
 Calcite 1.0 CO2(g) 1.3    # mineral from database, stoichiometric coefficient
 2e-3              # Add 1*2e-3 = 2e-3 mol Calcite and 1.3*2e-3 = 2.6e-3 mol CO2
END


# Example 3. Evaporate 99% of a HCl solution in 5 steps
#
SOLUTION 3
 pH   3.0 charge
 Cl   1.0
 water 1.0                     # 1 kg water = 55.51 mol
REACTION 3
 H2O -1.0
 54.951 moles in 5 steps
END
```

Notes

In example 1, the program recourses to the initial solution when adding the reaction steps. With keyword **INCREMENTAL_REACTIONS** true, the reaction steps are added cumulatively, thus giving 5e-3 and 15e-3 mol NaCl.

MIX

The effects of mixing of two or more groundwaters on the speciation and saturation state with respect to minerals can be calculated with keyword **MIX**. This keyword is also useful for simulating laboratory batch experiments.

```
# Example 1. Calculate mixing corrosion in limestone water
#
SOLUTION 1 Calcite saturated, high CO2
 pH  7.1  charge
 Ca  2.0  Calcite
 C(4) 4.0 CO2(g) -1.5
SOLUTION 2 Calcite saturated, low CO2
 pH  7.1  charge
 Ca  2.0  Calcite
 C(4) 4.0 CO2(g) -2.5
END
MIX 1
 1  0.4                        # use fraction 0.4 of solution 1
 2  0.6                        # use fraction 0.6 of solution 2
EQUILIBRIUM_PHASES 1
 Calcite                       # find how much calcite dissolves in the mixture
END


# Example 2. Evaporate 90% of 1 liter NaCl water, restore to 1 liter
#
SOLUTION 2
 Na 10
 Cl 10
REACTION 2
 H2O -1.0
 49.955                        # Evaporate 49.955 moles (= 0.9 * 55.506)
SAVE solution 3                # leaves 5.5506 mol H2O = 0.1 liter
END
MIX 3
 3 10    # Take fraction 10 of solution 3, is 10*5.5506 = 55.506 mol = 1 liter
END


# Example 3. Displace exchangeable cations with 1 M NaCl
#
SOLUTION 0  1M NaCl
 Na 1e3
 Cl 1e3
END
EXCHANGE 1 Fill centrifuge tube with 1 g clay = 1 mmol CEC
 KX 0.02e-3; MgX2 0.09e-3; CaX2 0.4e-3
MIX 1
 0 0.02                        # Add 20 ml of 1M NaCl solution
END
```

EXCHANGE

The keyword **EXCHANGE** is used to define exchange properties and to calculate the composition of the exchanger.

```
# Example 1. Calculate composition of an exchanger
#
SOLUTION 1
 Na   1.0
 K    0.2
 Cl   1.2
EXCHANGE 1
 X   30e-3              # 30 mmol X⁻
 -equil  1             # equilibrate with solution 1, --> 15 mmol NaX/L, 15 mmol KX/L
END


# Example 2. Input measured exchanger
#
EXCHANGE 1
 CaX2  20e-3           # 20 mmol exchangeable Ca
 NaX  10e-3            # 10 mmol exchangeable Na


# Example 3. Exchanger composition is calculated after reactions
#
SOLUTION 1-5
 Na  2.0
 C(4)  2.0 charge
EQUILIBRIUM_PHASES 1-5     # mineral equilibria for cells 1-5
 Calcite  0.0  0.01        # 0.01 mol Calcite, SI = 0.0
SAVE solution 1-5          # save equilibrated solutions
END

EXCHANGE 1-5               # exchangers for cells 1-5
 X  0.1                    # 0.1 mol X
 -equil  1
END
```

Notes
EXCHANGE defines moles of X^-, but the *concentration* depends on the amount of solution (default is 1 kg water). In example 1, the concentration is 30 mmol X^-/kg water.

In example 3, the exchanger is calculated with a mineral equilibrated solution, *after* **SAVE** and **END**. The calculation sequence is important here, the results are different when **EXCHANGE 1-5** is included before the first **END**. Any PHREEQC simulation starts with equilibration of the exchanger (if defined). Next, the reactions are calculated together with the exchanger. Here, the initial solution contains only Na^+, and the exchanger would be pure NaX. If the solution is then equilibrated with calcite, Ca^{2+} displaces Na^+ from the exchanger, and the Na^+ concentration in solution 1-5 will become higher than 2 mM.

The moles of an exchanger may be coupled to minerals (eq) or kinetic reactants (kine).

```
EXCHANGE 1-5
 X  Calcite eq  0.05          # X is coupled to calcite (an equilibrium phase)
                              # in proportion 0.05 mol X / mol calcite
```

Surface Complexation

PHREEQC contains the Dzombak and Morel database for surface complexation of heavy metal ions on hydrous ferric oxide (ferrihydrite, hfo). Ferrihydrite binds the metal ions and protons on strong and weak sites and develops a charge depending on the ions sorbed. The keyword **SURFACE** is used to define the surface complexation properties of sediments in much the same way as **EXCHANGE**, but since the surface may become charged, some precautions are in order.

```
# Example 1. Calculate the composition of a surface complex
#
SOLUTION 1
 Na  1.; Cl  1.; Zn  1e-3          # semicolon separates lines
SURFACE 1
 Hfo_w  2.4e-3  600  1.06          # 2.4e-3 mol weak sites, sp. surface = 600 m2/g
                                   # gram ferrihydrite = 1.06
 Hfo_s  6e-5                       # strong site, 6e-5 mol sites
 -equil  1                         # equilibrate with solution 1
END

# Example 2. Couple a surface with a mineral (eq) or kinetic reactant (kine)
#
SOLUTION 2                         # adjust pe to prevent (too much) Hfo dissolution
 pe  14 O2(g) -0.68                # pe is for P_O2 = 10^-0.68 = 0.21 atm
 Na  1.;  Cl  1.; Zn  1e-3
EQUILIBRIUM_PHASES 2
 Fe(OH)3(a)  0.0  1e-3
SAVE solution 2                    # Save solution 2 after equilibration
END
SURFACE 2
 Hfo_w  Fe(OH)3(a) eq 0.2 5.34e4 # weak sites, coupled to ferrihydrite,
                    # proportionality constant = 0.2, sp. surface = 5.34e4 m2/mol
 Hfo_s  Fe(OH)3(a) eq 0.005       # strong site, coupled to ferrihydrite,
                    # proportionality constant = 0.005
 -equil   3
END


# Example 3. An experiment: put 89 mg neutral HFO in 2 centrifuge tubes...
#
SURFACE 1-2
 Hfo_wOH  2e-4  600  0.089
 -diffuse_layer                    # neutralize surface with diffuse layer
END
#          1st tube, add 20 g of 10 mM HCl, react and decant in tube 2...
USE surface 1
SOLUTION 1
 pH  2.0 charge; Cl  10.0
 water 0.02                        # the solution has 0.02 kg water
SAVE solution 2
END
#          2nd tube...
USE surface 2; USE solution 2; SAVE solution 3
END
```

Notes
The default properties of HFO are: 89 g/mol, 600 m^2/g, 0.2 mol weak sites/mol, 0.005 mol strong sites/mol.

Make sure to have reactions calculated for a solution, to save it and to **END** the simulation, before equilibrating a surface as is done in example 2 (see also discussion in get-going sheet **EXCHANGE**).

When HFO is coupled to a mineral, the specific surface area is given in m^2/mol.

In example 3, HFO sorbs protons from the HCl solution and becomes positively charged. The charge is neutralized by Cl in the diffuse layer surrounding the particles. Thus, when the tube is decanted after centrifuging, the Cl concentration has decreased (how much? run the file...). This effect will be calculated with -diffuse_-layer true. (Default is -dif false). Diffuse layer calculations are computer intensive.

Two tips

• In rare cases, mainly with redox problems with very low concentrations of the metal ions, PHREEQC has difficulties finding a solution. The first trick is to include a redox buffer in the input file:

```
SOLUTION_SPECIES
 H2O + 0.01e- = H2O-0.01; log_k -9.0
```

• Titration to a fixed pH is illustrated in the following example.

```
# Determine Cd sorption edge on Hfo
PHASES
 Fix_ph                                # Define pH fixing mineral
 H+ = H+; log_k 0                      # pH = 10^(-SI)

SOLUTION 1
 pH 4.0; Na 100; Cl 100 charge; Cd 1e-3

SURFACE 1
 Hfo_w 0.2e-3 600 89e-3
 Hfo_s 0.05e-3
 -equil 1
END

USER_GRAPH
 -head pH %_cd_sor titrans
 -start
 10 sor = mol("Hfo_sOCd+") + mol("Hfo_wOCd+")  # 2 Cd surface complexes
 20 graph_x -la("H+")                           # pH on x-axis
 30 graph_y 100 * sor/(sor + tot("Cd"))         # % sorbed Cd on y-axis
# 40 graph_sy 1e6 * tot("Br")      # (to plot mol titrans on secondary y axis)
 -end
END

USE solution 1; USE surface 1
EQUILIBRIUM_PHASES 1
 Fix_ph -4.01 Na(OH)0.999999Br0.000001   # NaOH for increasing pH, with tracer Br
END
 USE solution 1; USE surface 1
 EQUILIBRIUM_PHASES 1; Fix_ph -4.5 Na(OH)0.999999Br0.000001
END
#  Etc. for pH up to 8...
```
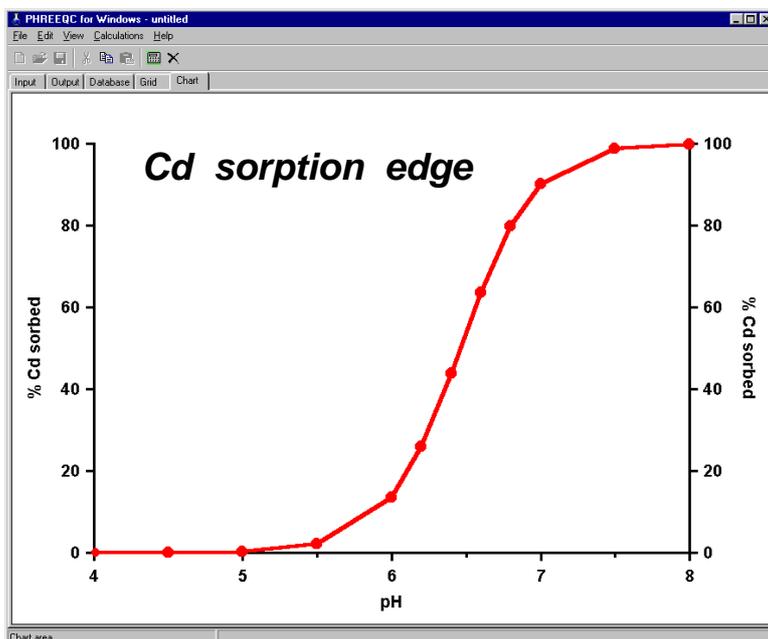
TRANSPORT

Keyword **TRANSPORT** is used for modeling 1D flowlines and laboratory columns. The flowline is divided in a number of cells 1-*n* for which **SOLUTION 1-*n*** must be defined. With advective flow, a *shift* moves water from each cell into the next, higher- or lower-numbered cell, depending on the flow direction.

```
# u_gex3 -- Transport and ion exchange: CaCl2 flushes column with (Na,K)NO3
#
SOLUTION 1-16  Initial solution in column
 Na  1.0; K  0.2; N(5) 1.2          # default pH, etc, note line separator ;
EXCHANGE 1-16
 X  1.1e-3;  -equilibrate 1
END
SOLUTION 0  Displacing solution, CaCl2
 Ca  0.6; Cl 1.2
END

PRINT; -reset  false                # suspend output
TRANSPORT
 -cells  16
 -length 0.005            # cell length 0.005 m, column length 16*0.005 = 0.08 m
 -dispersivity   0.002           # m
 -shifts 40                      # 40/16 = 2.5 pore volumes
 -flow_direction forward
 -time_step 720                  # 1 shift = 720 s. total time = 40*720 s
 -boundary_conditions flux flux  # at column ends
 -diffusion_coefficient 0.3e-9   # m2/s
 -punch 16                       # only punch/graph cell 16

USER_GRAPH
 -plot_concentration_vs time
 -start
 10 graph_x (step_no + 0.5)/cell_no  # transfer cell centered conc to column end
 20 graph_y tot("N"), tot("Cl"), tot("Na"), tot("K"), tot("Ca")
 -end
END
```
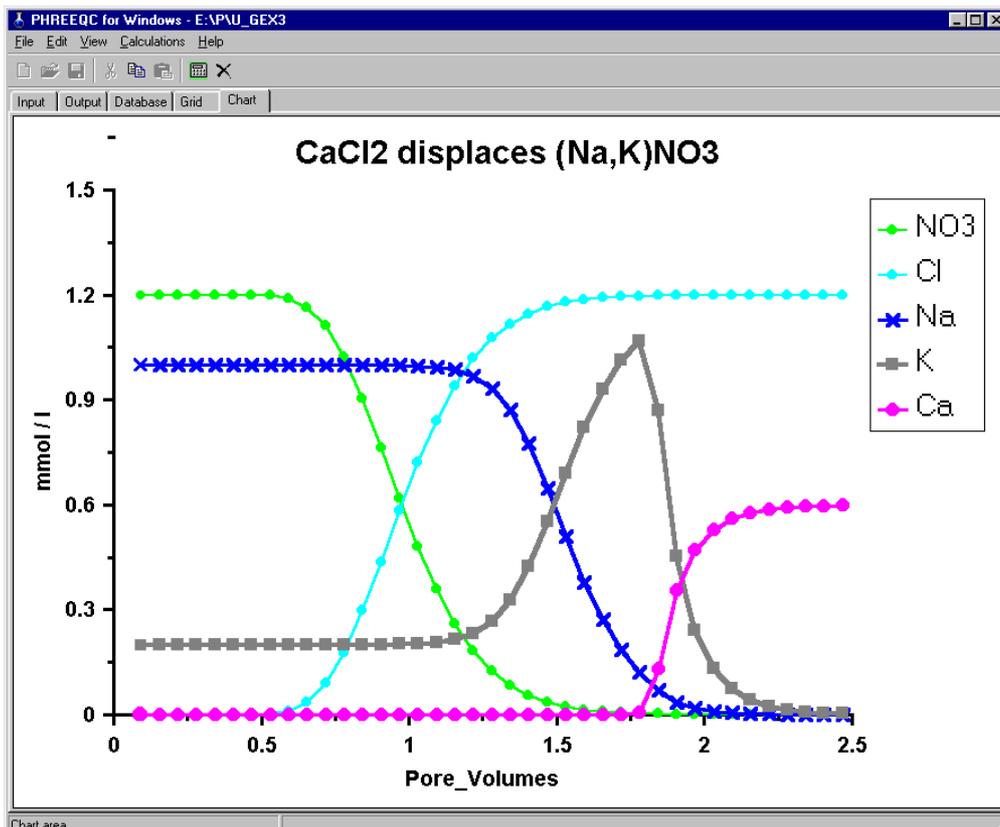
KINETICS

For kinetic calculations a rate equation must be programmed in BASIC using keyword **RATES**. The rate is called with keyword **KINETICS** which can also pass parameters to the rate. The BASIC functions are explained under keyword **RATES** in the PHREEQC manual.

```
#       Kinetic quartz dissolution
#
RATES
 Quartz                     # rate name
 -start
#1 rem  dQu/dt = -k * (1 - Ω_Quartz).  k = 10^-13.7 mol/m2/s (25 C)
#2 rem  parm(1) = A (m2), parm(2) = V (dm3) recalculate to mol/dm3/s

 10 moles = parm(1) / parm(2) * (m/m0)^0.67 * 10^-13.7 * (1 -  SR("Quartz"))
 20 save moles * time    # integrate. save and time must be in rate definition
                         # moles count positive when added to solution
 -end

KINETICS  # Sediment: 100% qu, grain size 0.1 mm, por 0.3, rho_qu 2.65 kg/dm3
 Quartz                      # rate name
 -formula SiO2
 -m0  102.7                  # initial moles of quartz
 -parms 22.7  0.162          # parameters for rate eqn. Here:
# Quartz surface area (m2/kg sediment), water filled porosity (dm3/kg sediment)
 -step 1.58e8 in 10 steps    # 1.58e8 seconds = 5 years
 -tol 1e-8                    # integration tolerance, default 1e-8 mol

INCREMENTAL_REACTIONS true  # start integration from previous step

SOLUTION 1

USER_GRAPH
 -heading time Si; -axis_titles years mmol/L
 -axis_scale y_axis 0 0.12 0.02; -axis_scale x_axis 0 5
 -start
 10 graph_x total_time/3.1536e7
 20 graph_y tot("Si")*1e3
 -end
END
```
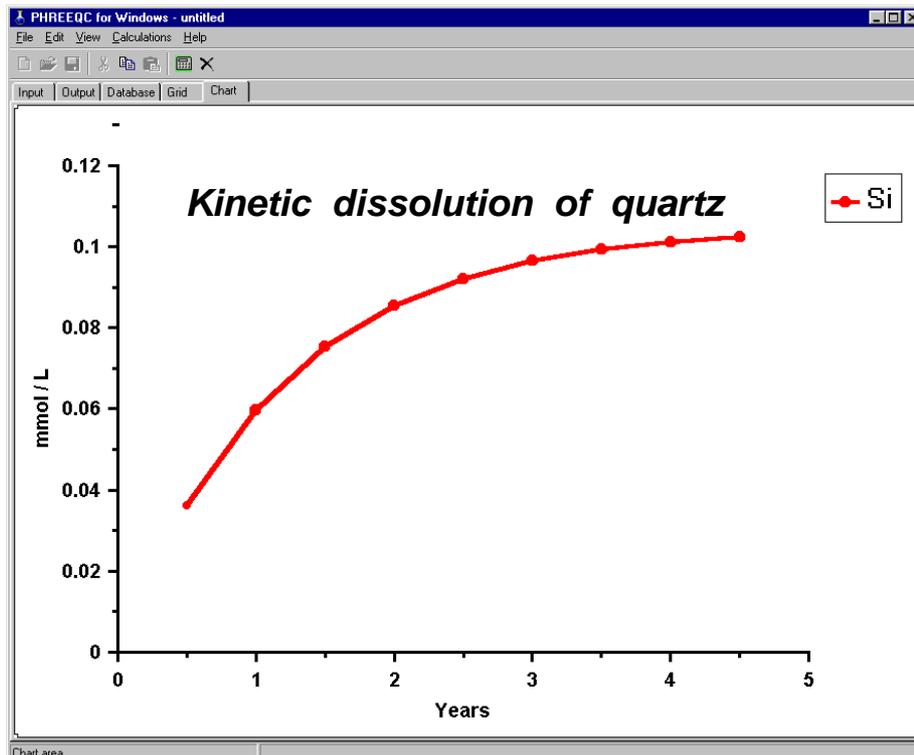
SOLID_SOLUTION

The solid solution option of PHREEQC can be used for modeling trace element behavior and is probably most useful for liquid solutions (BTEX etc., see Chapter 10). The solubility of the trace component in a solid solution is generally much smaller than when the trace element forms a pure solid. Consequently, the concentration of the minor component is much reduced in solution, and its mobility is diminished.

```
 SOLUTION 1
  pH   7.5  Calcite          # K = 10^-8.48
  C(4) 4.0
  Ca   1.0
  Cd   1 ug/kgw  Otavite      # Otavite = CdCO3, K = 10^-12.1
 SOLID_SOLUTION 1             # Note decrease of Cd concentration
  CaCdCO3
  -comp Calcite   0           # Ideal solid solution, initial amount = 0
  -comp Otavite   0
END


 USE solution 1
 SOLID_SOLUTION 1             # Regular solid solution with ideal properties
  CaCdCO3
  -comp1 Calcite   0
  -comp2 Otavite   0
# -distri   D1      D2       x1  x2      # D1=D2=D_ideal = K_cc/K_ot for all x
  -distri  4168.69 4168.69 0.1 0.6
END
```

Ideal solid solutions can have as many components as desired in PHREEQC, regular solid solutions have only two components. The properties of regular solid solutions can be defined by various means (in the example via distribution coefficients).

GAS_PHASE

This keyword is used to calculate equilibrium with a mixture of gases in a bubble. The bubble can have fixed volume and varying pressure, or it may have fixed total pressure and varying volume.

```
# Calculate CH4 gas formation under peat
#
SOLUTION 1
 pH 7.0 charge
 Ca 2.0 Calcite
 C(4) 2.0 CO2(g) -2.0          # P_CO2 = 0.01 atm
 S(6) 1.0
 N(0) 2.0  N2(g) 0.299         # P_N2 = 1.99 atm

REACTION 1
 CH2O 1; 0.01                  # decompose 10 mmol organic carbon

GAS_PHASE
 -fixed_pressure
 -pressure 2.0                 # 2 atm, at 10 m depth
 -volume 1e-8                  # negligible initial volume, 1e-8 liter
 -temperature  25              # default 25 C
 CH4(g)  0.0                   # gas name from PHASES, partial pressure
 H2S(g)  0.0
 CO2(g)  0.005
 N2(g)   0.995
END
```

Databases

Currently 4 databases are provided with PHREEQC, PHREEQC.DAT is the smallest. WATEQ4F.DAT has additional data for heavy metals, MINTEQ.DAT has a few more organic chemicals, and LLNL.DAT is a huge database with many minerals and large-range, temperature dependent equilibrium constants. The databases contain lists under keywords.

```
SOLUTION_MASTER_SPECIES                                # always needed
#element  species   alk      gfw_formula    element_gfw
H         H+        -1.0     H              1.008
H(0)      H2        0.0      H
H(1)      H+        -1.0     0.0
E         e-        0.0      0.0            0.0
O         H2O       0.0      O              16.0
O(0)      O2        0.0      O
O(-2)     H2O       0.0      0.0
# ...the above elements must always be present in the database
Ca        Ca+2      0.0      Ca             40.08
Fe        Fe+2      0.0      Fe             55.847   # Fe+2 is primary redox species
Fe(+2)    Fe+2      0.0      Fe
Fe(+3)    Fe+3      -2.0     Fe
# The primary species reaction is repeated in SOLUTION_SPECIES, with log_k = 0
# etc...
SOLUTION_SPECIES
H+ = H+                               # H+ primary species
        log_k    0.0
        -gamma   9.0      0.0    # params for activity coefficient
Fe+2 = Fe+2                           # Fe+2 is the primary redox species for Fe
        log_k    0.0
        -gamma   6.0      0.0
Fe+2 = Fe+3 + e-                      # new species defined on the right of = sign
        log_k    -13.02
        delta_h 9.680     kcal  # temp. dependency from Van 't Hoff eqn
        -gamma   9.0      0.0
# etc...
PHASES                               # Minerals
Calcite
 CaCO3 = CO3-2 + Ca+2
        log_k    -8.48
        delta_h -2.297 kcal
        -analytic  -171.9065  -0.077993  2839.319  71.595   # log_k vs temp
# etc...
EXCHANGE_MASTER_SPECIES
 X        X-                          # element, species
EXCHANGE_SPECIES
 X- = X-                              # reaction for master species with log_k = 0
        log_k    0.0
 Na+ + X- = NaX
        log_k    0.0
        -gamma   4.0      0.075
# etc...
SURFACE_MASTER_SPECIES               # element, species
 Hfo_s    Hfo_sOH
 Hfo_w    Hfo_wOH
SURFACE_SPECIES
 Hfo_sOH = Hfo_sOH                    # reaction for master species with log_k = 0
        log_k    0.0
 Hfo_sOH + H+ = Hfo_sOH2+
        log_k    7.29                 # = pKa1,int
# etc...
RATES
# etc...
END
```

INVERSE_MODELING

Inverse modeling aims to decipher the reactions and mixtures which have led to a given water quality.

```
# Find the reactions which produced solution 2 from solution 1.
#
 PRINT; -reset false; inverse true
 SOLUTION 1
  Cl 1;  Na 1
# evaporate 90% of solution 1, then add 2 mM gypsum
 SOLUTION 2
  Cl 10;  Na 10;  Ca   2;  S(6) 2
END

 INVERSE_MODELING
  -solutions 1 2          # Balance solution 2 from 1
  -phases                 # Using reactants from PHASES
   Gypsum
   Water                  # Water not in PHASES in database, is defined below

  -balances               # Any elements not in phases
   Cl                     # Add 0   0.05 uncertainty for absolute balance of Cl
   Na
   Alkalinity 1           # Permitted uncertainty 100%

  -uncertainty 0.05       # Default uncertainty, 5%

  -range true

 PHASES
  Water                   # Define water
  H2O = H2O
  log_k 0                 # log K not used
END
```

With the identifier -phases the possibly reacting phases are indicated. All reactants must have been defined either as **EXCHANGE_SPECIES** or under keyword **PHASES**. These 'phases' are used only for mole balancing, their log K is unimportant when they are used in **INVERSE_MODELING**.

Elements which are not a part of the indicated phases, but are present in the solutions, must be listed with -balances, as done for Na, Cl and alkalinity in this example. Numbers after the elements indicate the permitted uncertainty for the solutions (in the order entered with identifier -solutions). A positive number indicates fractional uncertainty, a negative number means that the uncertainty, in mol/kgw, may increase up to the absolute value of the number. In the example, the permitted uncertainty for the alkalinity is set to 100% of the input concentration. The alkalinity is very small for these two solutions, and a balance can not be obtained without allowing for a large uncertainty.

Isotopes can be included in inverse models, the δ values are entered under **SOLUTION**.