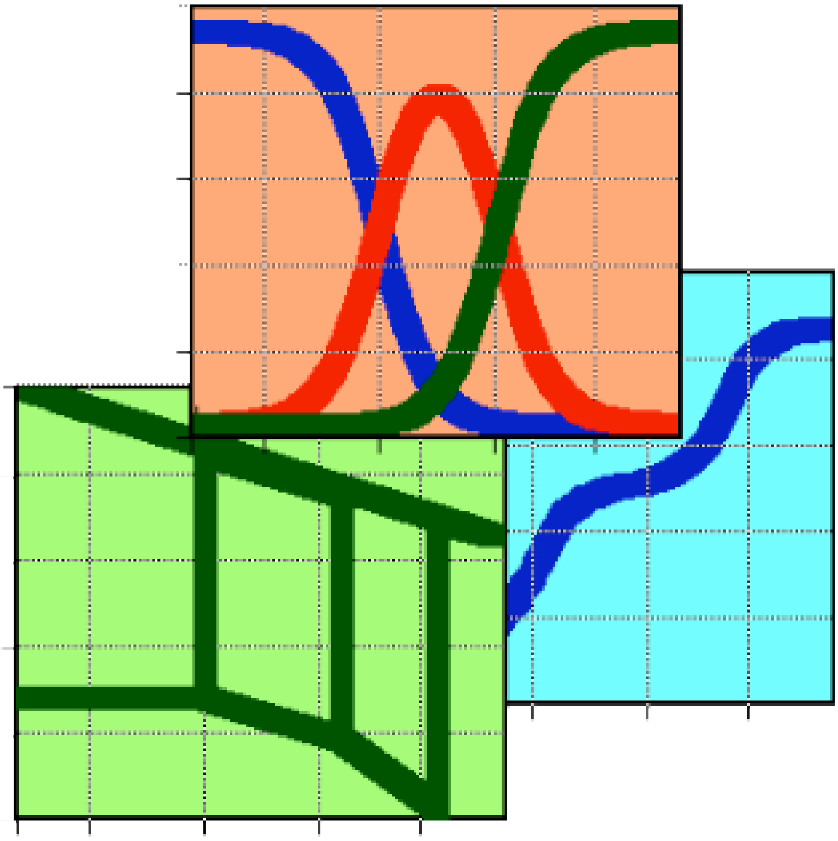
MANUAL

ChemEQL

V3.2

A Program to Calculate Chemical Speciation Equilibria,
Titrations, Dissolution, Precipitation, Adsorption,
Kinetics, pX-pY Diagrams, Solubility Diagrams.
Libraries with Complexation Constants
For MacOSX, Windows, Linux, Solaris



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The Program

ChemEQL, insinuating ‘Chemical Equilibrium’*,* calculates and draws thermodynamic equilibrium concentrations of species in complex chemical systems. It handles homogeneous solutions, dissolution, precipitation, titration with acid or other components. Adsorption on up to five different particulate surfaces can be calculated with the choice of the Constant Capacitance, Diffuse Layer (Generalized Two Layer), Basic Stern Layer, or Triple Layer model to consider for surface charges. Corrections for ionic strength can be made and activities calculated. One rate determining process in a system of otherwise fast thermodynamic chemical equilibrium can be simulated. Two-dimensional logarithmic diagrams, such as pε-pH, can be calculated. A simple drawing option is provided. A library with over 1700 thermodynamic stability constants allows quick access and easy use of the program. Another library with more than 300 solubility constants allows easy introduction of solid phases.

The present application was developed starting out from the original program MICROQL in BASIC by John Westall. The basic principles of the calculation method is documented by J. Westall, "Chemical Equilibrium Including Adsorption on Charged Surfaces", Advances in Chemistry Series, no. 189, Particulates in water, ed. by M.C. Kavanaugh and J.O. Leckie, 1980, and J. Westall, J.L. Zachary and F. Morel, "MINEQL, a Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems", Technical Note no. 18, Ralph M. Parsons Lab. MIT, Cambridge, 1976.

Kai-H. Brassel (www.vseit.de) implemented this program in Java code. Independent from whether you work under Windows, Linux, Solaris or MacOS X (for older operating systems there exists a Pascal-version of ChemEQL) the application can be downloaded from

http://www.eawag.ch/research/surf/forschung/chemeql.html

By clicking on the ChemEQL icon the application is downloaded, installed on your hard disc, and started. Installation is made independent from your operating system directly from the internet browser through the WebStart-plugin from Sun Microsystems Inc. (www.sun.com). WebStart cares for the installation of a suitable Java runtime environment in case it is not available, and for the automatic installation of new versions of ChemEQL. In case WebStart is not yet installed or part of the operating system (as in MacOS X) WebStart will be installed automatically as Browser-Plugin first from the Java WebStart setup page of Sun Microsystems, Inc. The installation is a one-time process. The ChemEQL application launched with Java WebStart is cached locally on your hard disk and works off-line.

A manual can be downloaded that intends to be a practical guide through most options the program offers. I believe that providing examples makes it easier to pick things up that explaining theory.

Kastanienbaum, May 1, 2015 Beat Müller

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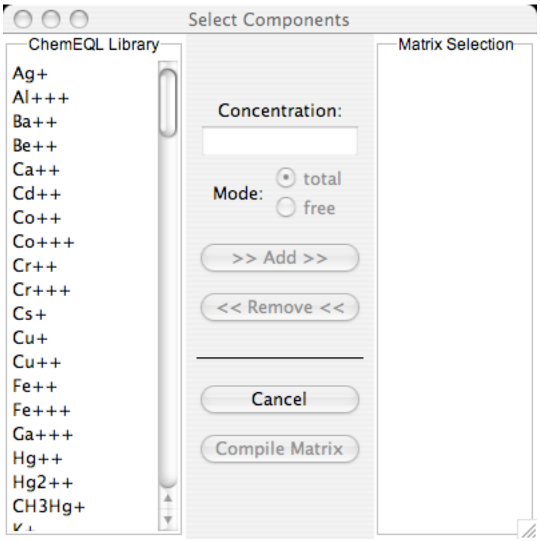
Content

Jump Start

Set up a matrix

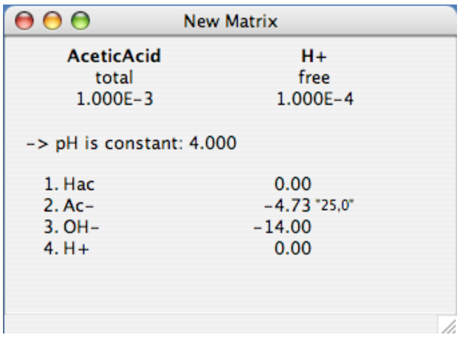
Putting up a matrix by hand is a source of many mistakes and sometimes it is quite a task to find species, reactions, and stability constants. Two libraries are provided for the users comfort, one containing complex formation constants and the other solubility products. Both libraries are automatically downloaded, digitalized and stored in the users home account. At startup, the program checks the availability of the users libraries. In case they are missing, changed names, or were deleted the program reloads the libraries again. Hence, you are not bothered by the installation or preparation of the libraries.

Starting the ChemEQL application you will find the ***Access Library...*** item under the ***File*** menu. The following window will appear:



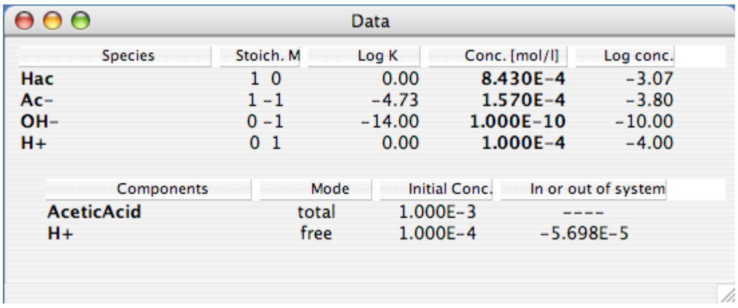
In the list to the left you see the content of the library components, the list to the right is now empty and will show the components that you have selected. Activate a component by mouse click, enter its concentration, choose the mode (either '**total**' to indicate that the number means the total concentration of that component in your system, or '**free**' if the input refers to the concentration of the individual species selected, e.g. pH. In the latter case the free concentration of this species will be held constant). Clicking the '**>>Add>>**' button (or CR) will remove the selected component from the library and transfer it to your selection. If you wish to remove a component from your selection, activate it and press the now active '**<<Remove<<**' button. The component will be removed from the selection and added at the end of the library list.

As an example we want to perform some pH and concentration calculations with diluted acetic acid: In order to select the matrix for the acetic acid system (which we will put up in detail with much effort on pages 29-31), select '**AceticAcid**' from the library, enter '**1e-3**' for concentration, and press the '**Add**' button. Proceed to the end of the library list, select '**H+**', enter '**1e-4**' for the concentration, choose '**free**' (since we want to calculate for constant pH), and press again the '**Add**' button. This is the whole selection needed. Pressing '**compile matrix**' will end the library dialog. The program will search the library for all possible combinations of the chosen components and will list them as species. (There is no guarantee for completeness!). The following window will appear and show the components you selected with the concentration and mode, and all species that were found in the library with the attached formation constants.



```
      AceticAcid                 H+
        total                   free
      1.000E-3                1.000E-4

 -> pH is constant: 4.000

   1. Hac                     0.00
   2. Ac-                    -4.73 "25,0"
   3. OH-                   -14.00
   4. H+                      0.00
```

If you wish to use this matrix again make sure to save it: Choose ***Save Matrix...*** from the ***File*** menu! ***Run*** and ***Go*** will calculate the speciation of that system: What are the concentrations of HAc and Ac- in a solution of pH 4?



Species	Stoich. M	Log K	Conc. [mol/l]	Log conc.
Hac	1 0	0.00	**8.430E-4**	-3.07
Ac-	1 -1	-4.73	**1.570E-4**	-3.80
OH-	0 -1	-14.00	**1.000E-10**	-10.00
H+	0 1	0.00	**1.000E-4**	-4.00

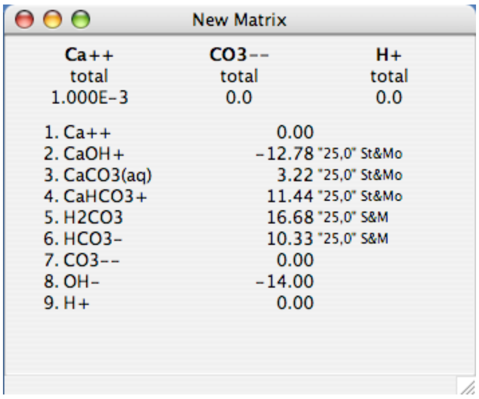
Components	Mode	Initial Conc.	In or out of system
AceticAcid	total	1.000E-3	----
H+	free	1.000E-4	-5.698E-5

The upper part of the data window lists the **species**, the **stoichiometric matrix**, the **formation constants** used, the **equilibrium concentrations** and their **logarithms**. The lower part describes the **components** (which must be in the species list as well), their **mode** and **initial concentration**. The '**in or out of system**' column gives the amount (per liter) of a component that had to be added to or taken away from a system in order to keep its free concentration constant during a process. In this example the value of '-5.698e-5' means that this concentration of H^+ had to be neutralized in the system (taken out) in order to keep up a pH of 4 when preparing a solution of 10^{-3} M acetic acid.

Insert solid phases

Setting up a matrix to calculate dissolution of a solid phase (with an unlimited concentration) or to check whether precipitation of a solid phase occurs from a solution of a certain composition (limited concentration) takes two steps:

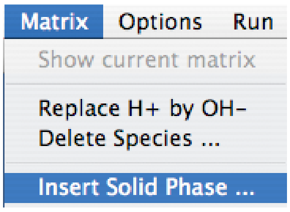
1 st Create a matrix from the library containing the metal ion(s) and the ligand(s), which together form the solid phase, eg. if we want to investigate dissolution of $CaCO_3$ (Calcite) in pure water select the components ‘Ca++’, ‘CO3--‘ and ‘H+’:



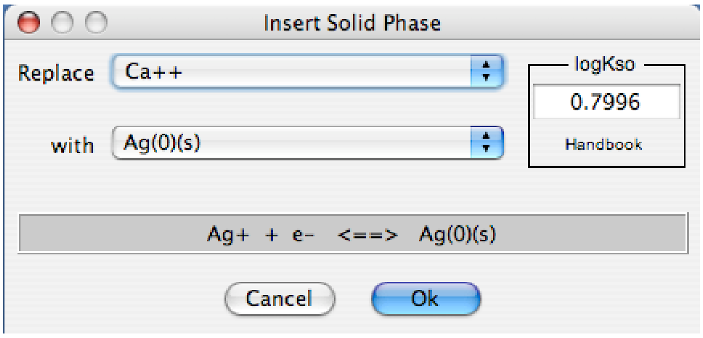
```
   Ca++          CO3--          H+
   total         total          total
   1.000E-3      0.0            0.0

1. Ca++             0.00
2. CaOH+          -12.78 "25,0" St&Mo
3. CaCO3(aq)        3.22 "25,0" St&Mo
4. CaHCO3+         11.44 "25,0" St&Mo
5. H2CO3           16.68 "25,0" S&M
6. HCO3-           10.33 "25,0" S&M
7. CO3--            0.00
8. OH-            -14.00
9. H+               0.00
```

(The concentration of the cation is of no importance and will be set to 1 later automatically when transformed into solid phases.)

2nd The next steps are to replace 'Ca++' by Calcite. This is done with the help of the solid phases library. It is accessed with the item ***Insert Solid Phases...*** from the ***Matrix*** menu. (To change or extend this library see next chapter):



The following window will appear:



Replace Ca++

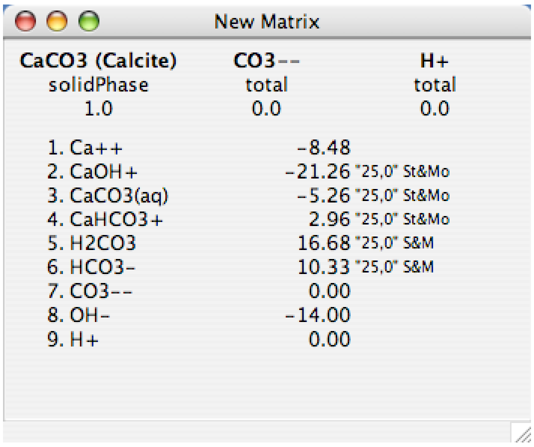
with Ag(0)(s)

logKso 0.7996

Handbook

Ag+ + e- <==> Ag(0)(s)

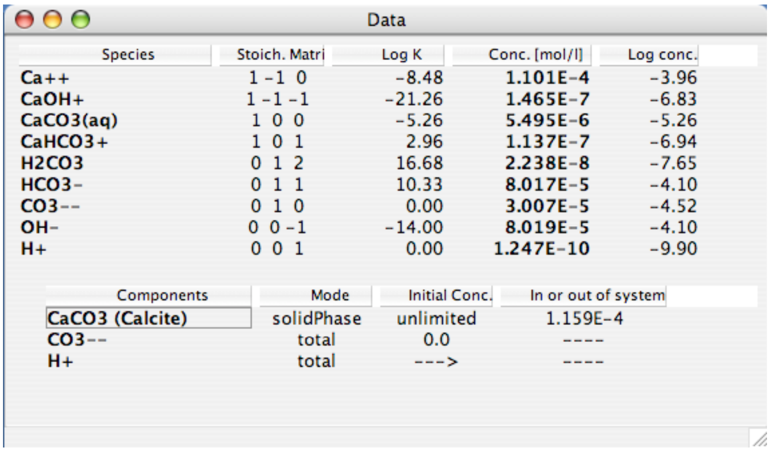
Now replace **'Ca++'** with **$CaCO_3$ (Calcite)** by scrolling down the pop up menu ‘with’. The current matrix will be recalculated for the solid phase to:



CaCO3 (Calcite)	CO3--	H+
solidPhase	total	total
1.0	0.0	0.0

1. Ca++	-8.48
2. CaOH+	-21.26 "25,0" St&Mo
3. CaCO3(aq)	-5.26 "25,0" St&Mo
4. CaHCO3+	2.96 "25,0" St&Mo
5. H2CO3	16.68 "25,0" S&M
6. HCO3-	10.33 "25,0" S&M
7. CO3--	0.00
8. OH-	-14.00
9. H+	0.00

As you can see, the mode is now **‘solidPhase’**, and the activity is set =1 as defined for solid phases. Starting the calculation will lead to the composition of the system where calcite is in equilibrium with pure water. In order to reach this equilibrium $1.16 \cdot 10^{-4}$ mol calcite were dissolved per liter of solution.

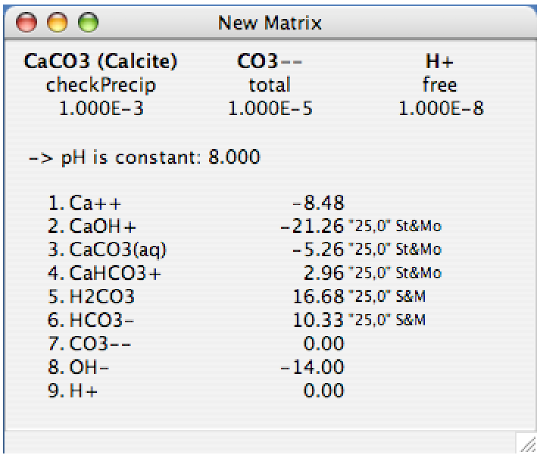


Species	Stoich. Matri	Log K	Conc. [mol/l]	Log conc.
Ca++	1 -1 0	-8.48	1.101E-4	-3.96
CaOH+	1 -1 -1	-21.26	1.465E-7	-6.83
CaCO3(aq)	1 0 0	-5.26	5.495E-6	-5.26
CaHCO3+	1 0 1	2.96	1.137E-7	-6.94
H2CO3	0 1 2	16.68	2.238E-8	-7.65
HCO3-	0 1 1	10.33	8.017E-5	-4.10
CO3--	0 1 0	0.00	3.007E-5	-4.52
OH-	0 0 -1	-14.00	8.019E-5	-4.10
H+	0 0 1	0.00	1.247E-10	-9.90

Components	Mode	Initial Conc.	In or out of system
CaCO3 (Calcite)	solidPhase	unlimited	1.159E-4
CO3--	total	0.0	----
H+	total	--->	----

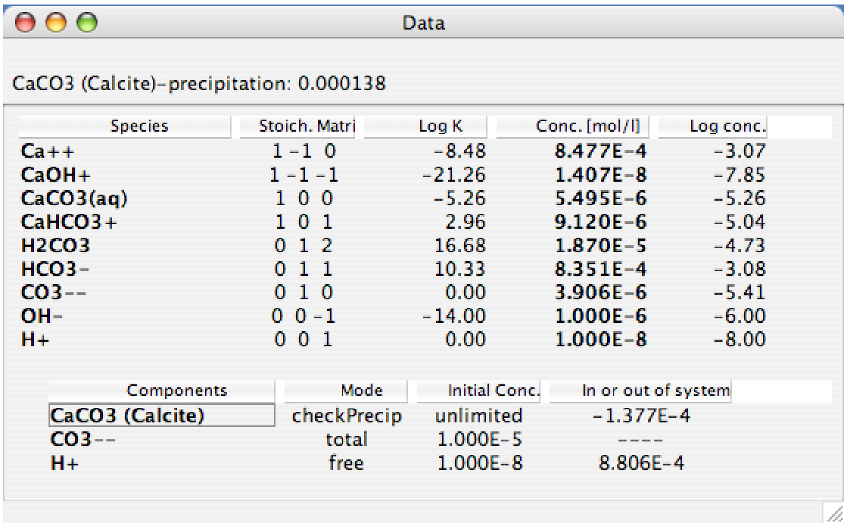
Check for precipitation

A different task is to check whether calcite precipitates from a solution of a certain composition, e.g. 10^{-3} mol/l Ca^{2+} and 10^{-5} mol/l CO_3^{2-} at pH 8. The same matrix can be used changing the modes of calcite from **solidPhase** to **checkPrecip** and entering the concentration of total dissolved Ca (the sum of all dissolved Ca species), total dissolved carbonate (the sum of all carbon species) and fixed pH. All these changes can be entered interactively in the matrix window: The matrix should then look the following way:



```
CaCO3 (Calcite)      CO3--        H+
  checkPrecip        total       free
   1.000E-3        1.000E-5    1.000E-8

-> pH is constant: 8.000

  1. Ca++                 -8.48
  2. CaOH+               -21.26 "25,0" St&Mo
  3. CaCO3(aq)            -5.26 "25,0" St&Mo
  4. CaHCO3+               2.96 "25,0" St&Mo
  5. H2CO3                16.68 "25,0" S&M
  6. HCO3-                10.33 "25,0" S&M
  7. CO3--                 0.00
  8. OH-                 -14.00
  9. H+                    0.00
```

The result window shows that such a solution is oversaturated with respect to calcite: $1.38 \cdot 10^{-4}$ mol of calcite was precipitated from one liter of solution (also under ‘in or out of system’), and the composition of the solution is given:



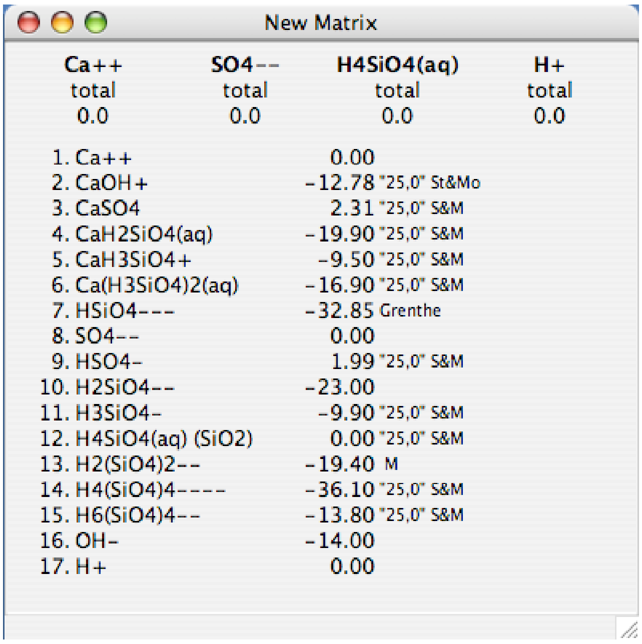
```
CaCO3 (Calcite)-precipitation: 0.000138

   Species          Stoich. Matri    Log K     Conc. [mol/l]   Log conc.
Ca++                  1 -1  0        -8.48      8.477E-4        -3.07
CaOH+                 1 -1 -1       -21.26      1.407E-8        -7.85
CaCO3(aq)             1  0  0        -5.26      5.495E-6        -5.26
CaHCO3+               1  0  1         2.96      9.120E-6        -5.04
H2CO3                 0  1  2        16.68      1.870E-5        -4.73
HCO3-                 0  1  1        10.33      8.351E-4        -3.08
CO3--                 0  1  0         0.00      3.906E-6        -5.41
OH-                   0  0 -1       -14.00      1.000E-6        -6.00
H+                    0  0  1         0.00      1.000E-8        -8.00

     Components           Mode      Initial Conc.   In or out of system
  CaCO3 (Calcite)     checkPrecip    unlimited         -1.377E-4
  CO3--                  total       1.000E-5            ----
  H+                     free        1.000E-8          8.806E-4
```

Several solid phases

The procedure is the same as in the former case. Set up a matrix from the library that contains the cation and all the ligands that will occur in the solid phases. In a second step, the solid phases will be introduced from the solid phase library.

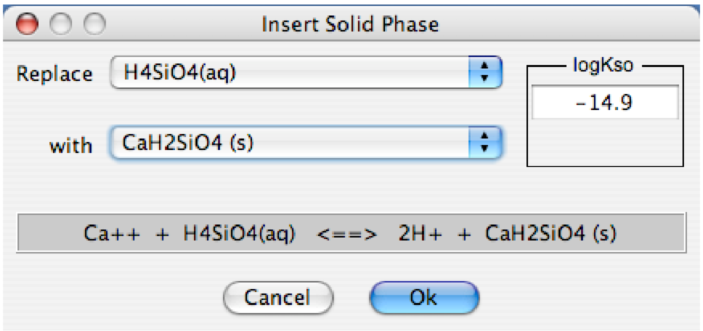
Example: What is the solubility of $CaSO_4$(s) and CaH_2SiO_4(s) in pure water.

Procedure: Select **Ca++**, **SO4--**, **H4SiO4**, and **H+** from the library to obtain the following matrix:



```
    Ca++          SO4--       H4SiO4(aq)        H+
    total         total         total          total
     0.0           0.0           0.0            0.0

  1. Ca++                    0.00
  2. CaOH+                 -12.78 "25,0" St&Mo
  3. CaSO4                   2.31 "25,0" S&M
  4. CaH2SiO4(aq)          -19.90 "25,0" S&M
  5. CaH3SiO4+              -9.50 "25,0" S&M
  6. Ca(H3SiO4)2(aq)       -16.90 "25,0" S&M
  7. HSiO4---              -32.85 Grenthe
  8. SO4--                   0.00
  9. HSO4-                   1.99 "25,0" S&M
 10. H2SiO4--              -23.00
 11. H3SiO4-                -9.90 "25,0" S&M
 12. H4SiO4(aq) (SiO2)       0.00 "25,0" S&M
 13. H2(SiO4)2--           -19.40  M
 14. H4(SiO4)4----         -36.10 "25,0" S&M
 15. H6(SiO4)4--           -13.80 "25,0" S&M
 16. OH-                   -14.00
 17. H+                      0.00
```

(The concentration for Ca++ is irrelevant and will be set to 1 automatically when solid phases are introduced). Solid phases can now be inserted. Firstly, **H4SiO4(aq)** is replaced with **CaH2SiO4(s)**



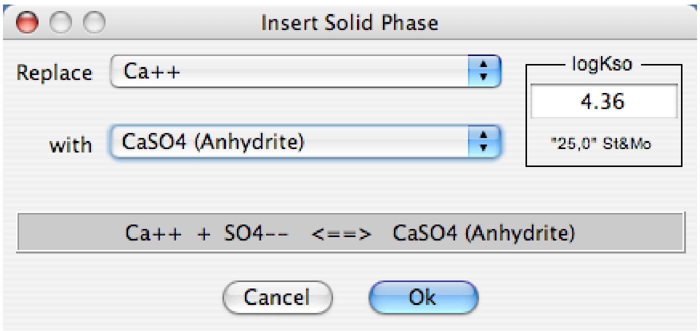
Replace H4SiO4(aq)

with CaH2SiO4 (s)

logKso -14.9

Ca++ + H4SiO4(aq) <==> 2H+ + CaH2SiO4 (s)

The order in which the solid phases are inserted is not important. We could have replaced **SO4--** by **CaSO4(s)** first as well. ***However, the ligand components have to be replaced first, and the metal component last!*** Now we replace **Ca++** by **CaSO4 (Anhydrite)**:



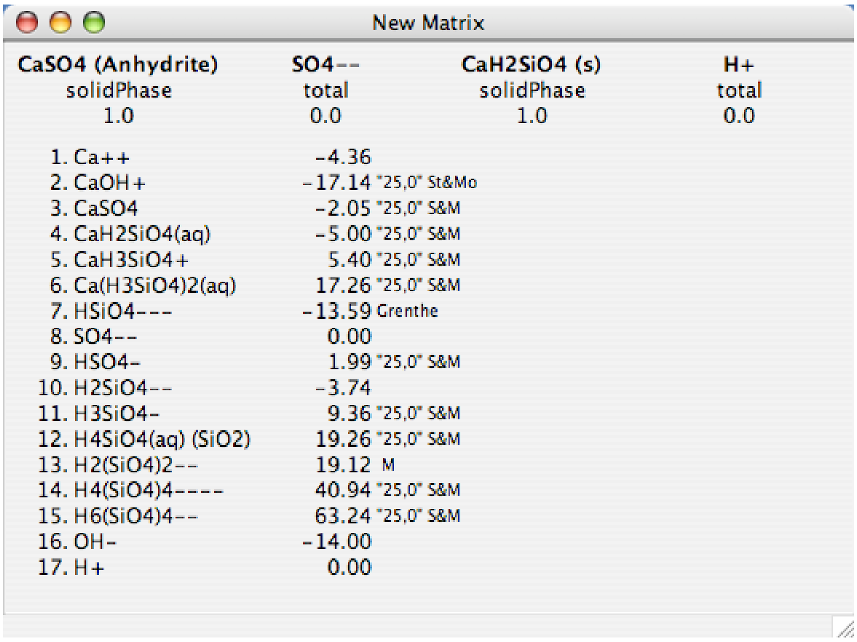
Replace: Ca++

with: CaSO4 (Anhydrite)

logKso: 4.36 "25,0" St&Mo

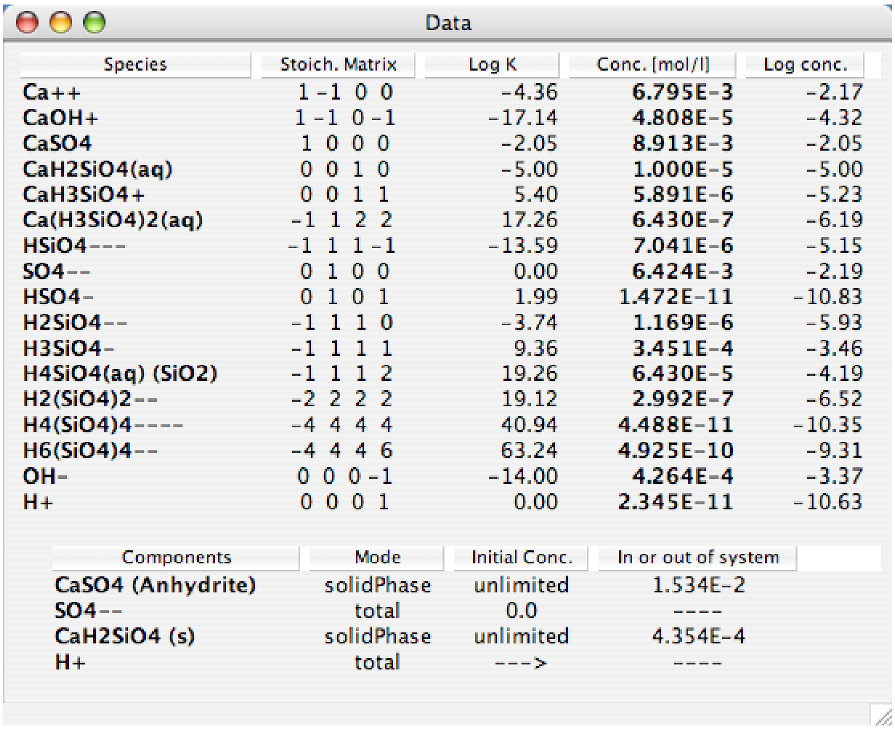
Ca++ + SO4-- <==> CaSO4 (Anhydrite)

The following matrix is obtained with new stoichiometric coefficients and recalculated complexation constants:



```
CaSO4 (Anhydrite)        SO4--         CaH2SiO4 (s)       H+
   solidPhase            total          solidPhase       total
      1.0                 0.0              1.0            0.0

  1. Ca++                 -4.36
  2. CaOH+               -17.14 "25,0" St&Mo
  3. CaSO4                -2.05 "25,0" S&M
  4. CaH2SiO4(aq)         -5.00 "25,0" S&M
  5. CaH3SiO4+             5.40 "25,0" S&M
  6. Ca(H3SiO4)2(aq)      17.26 "25,0" S&M
  7. HSiO4---            -13.59 Grenthe
  8. SO4--                 0.00
  9. HSO4-                 1.99 "25,0" S&M
 10. H2SiO4--             -3.74
 11. H3SiO4-               9.36 "25,0" S&M
 12. H4SiO4(aq) (SiO2)    19.26 "25,0" S&M
 13. H2(SiO4)2--          19.12  M
 14. H4(SiO4)4----        40.94 "25,0" S&M
 15. H6(SiO4)4--          63.24 "25,0" S&M
 16. OH-                 -14.00
 17. H+                    0.00
```

The result of the calculation shows that $CaSO_4$ (Anhydrite) is more soluble than CaH_2SiO_4 since $1.53{\cdot}10^{-2}$ moles of Anhydrite per liter were dissolved, and only $4.35{\cdot}10^{-4}$ moles of calcium silicate:



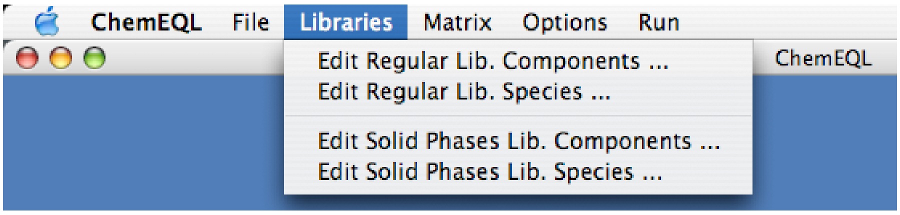
Data

Species	Stoich. Matrix	Log K	Conc. [mol/l]	Log conc.
Ca++	1 -1 0 0	-4.36	6.795E-3	-2.17
CaOH+	1 -1 0 -1	-17.14	4.808E-5	-4.32
CaSO4	1 0 0 0	-2.05	8.913E-3	-2.05
CaH2SiO4(aq)	0 0 1 0	-5.00	1.000E-5	-5.00
CaH3SiO4+	0 0 1 1	5.40	5.891E-6	-5.23
Ca(H3SiO4)2(aq)	-1 1 2 2	17.26	6.430E-7	-6.19
HSiO4---	-1 1 1 -1	-13.59	7.041E-6	-5.15
SO4--	0 1 0 0	0.00	6.424E-3	-2.19
HSO4-	0 1 0 1	1.99	1.472E-11	-10.83
H2SiO4--	-1 1 1 0	-3.74	1.169E-6	-5.93
H3SiO4-	-1 1 1 1	9.36	3.451E-4	-3.46
H4SiO4(aq) (SiO2)	-1 1 1 2	19.26	6.430E-5	-4.19
H2(SiO4)2--	-2 2 2 2	19.12	2.992E-7	-6.52
H4(SiO4)4----	-4 4 4 4	40.94	4.488E-11	-10.35
H6(SiO4)4--	-4 4 4 6	63.24	4.925E-10	-9.31
OH-	0 0 0 -1	-14.00	4.264E-4	-3.37
H+	0 0 0 1	0.00	2.345E-11	-10.63

Components	Mode	Initial Conc.	In or out of system
CaSO4 (Anhydrite)	solidPhase	unlimited	1.534E-2
SO4--	total	0.0	----
CaH2SiO4 (s)	solidPhase	unlimited	4.354E-4
H+	total	--->	----

Access the libraries

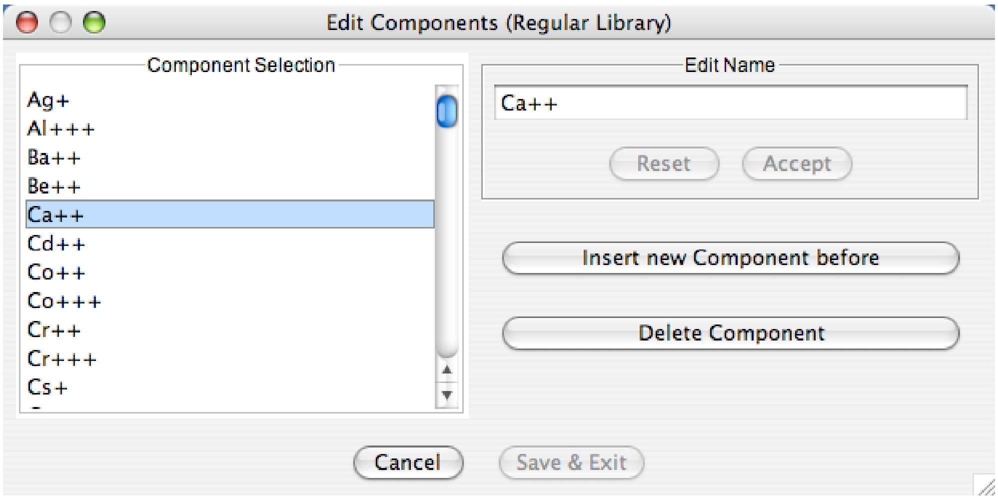
You can add your own components, species and complex formation constants to the existing libraries, delete species and components or change their names and constants. All facilities needed are given in the ***Libraries*** menu:



The ***Regular Library*** contains mass action laws and formation constants of ***dissolved*** species, the ***Solid Phases Library*** solubility products. Access to the solid phases library is organized in precisely the same way as for the regular library, hence, only the management of the Regular Library will be presented here.

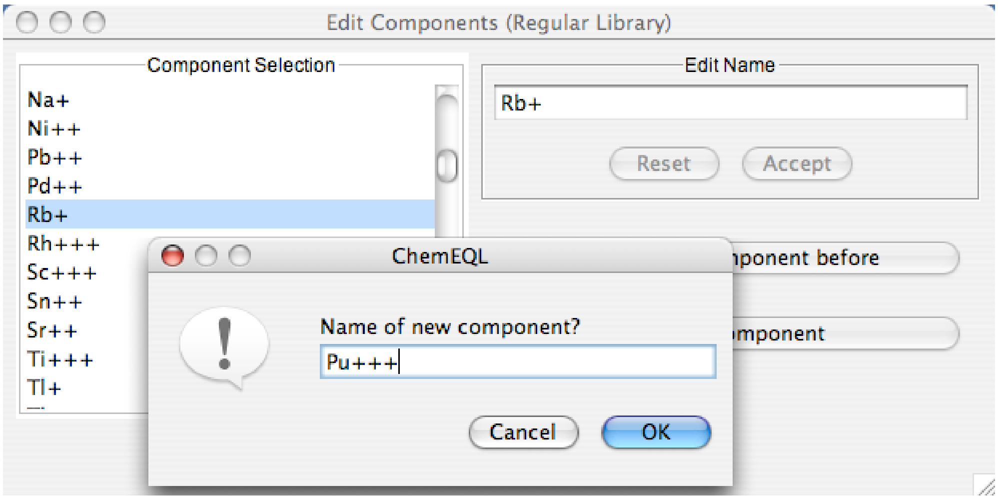
Edit Regular Library Components

This dialog handles the **insertion of new components** or the **deletion of components** in the regular Library. **Component names can be changed** as well here:



Edit Name: Ca++

New components are entered after pressing the **'Insert new component before'** bar. Place the new component alphabetically in the library. E.g. insertion of Pu^{3+} is made in the following way:



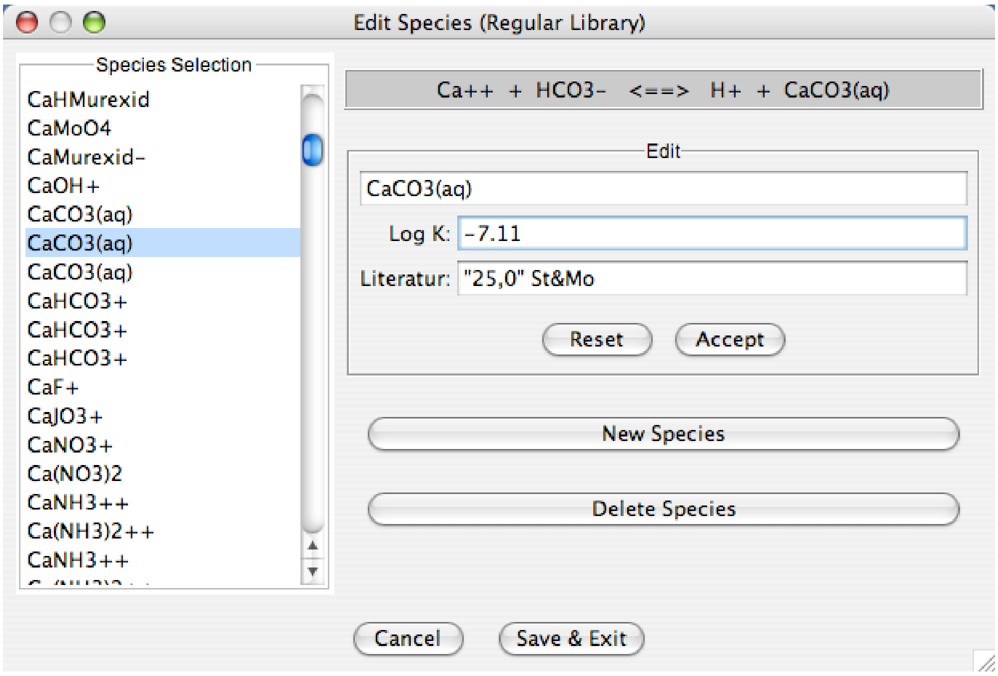
Edit Name: Rb+

Name of new component? Pu+++

Prevent an inflation of new components! Check if the formation of a new species possibly can be written with an already existing component, e.g. with SO4-- instead of HSO4-. New components do not need to be introduced as species explicitly. This is done automatically.

Edit Regular Library Species

The next dialog gives access to the **names of species**, their **binding constants** and **literature**. *Always use the **FORMATION constant** of the species!* The top right gray field lists the mass action law for which the binding constant is valid:



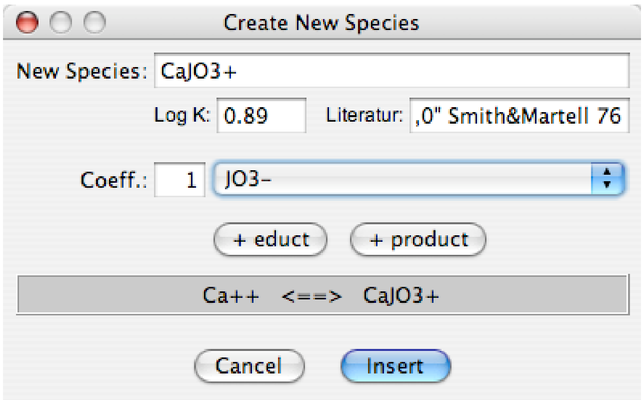
Ca++ + HCO3- <==> H+ + CaCO3(aq)

CaCO3(aq)

Log K: -7.11

Literatur: "25,0" St&Mo

Species can be ***deleted***. New species can be ***inserted*** with their mass action law, complex formation constant, Literature including temperature and ionic strength where they are valid, by pressing the **‘New Species’** bar. To insert a new species, e.g. $CaJO_3^+$, write its name in the first field. This name will appear on the product side in the gray text field below showing the mass action law. Then write its **FORMATION** equation using the **popup menu with all the components** offered from the respective library. Select an educt or product component and direct it to the educt or product side of the mass law equation shown in the gray field below with the respective buttons. The **'Lit.'** field takes notes for temperature, ionic strength and literature references but can remain empty. To be compatible with the present style write ‘“***Temp,ionic strength***” **Lit**’. New species are added in alphabetical order starting from the beginning of the library.



New Species: CaJO3+

Log K: 0.89

Literatur: „0" Smith&Martell 76

Coeff.: 1 JO3-

Ca++ <==> CaJO3+

The **regular library** at present contains data of more than 100 components and more than 1700 species. The **solid phases-library** holds 68 components and more than 300 species.

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Appelo&Postma C.A.J. Appelo and D. Postma, 1993. Geochemistry, groundwater and pollution. Balkema, Rotterdam, NL. pp.536.

Baes&Mesmer	C.F. Baes, R.E. Mesmer, 1986. The hydrolysis of cations. Robert E. Kreiger Publishing Company, Malabar FL. pp.489.
Basset	R.L. Bassett, 1980. A critical evaluation of the thermodynamic data for boron ions, ion pairs, complexes, and polyanions in aqueous solution at 298.15 K and 1 bar. Geochim Cosmochim Acta, 44, 1151-1160.
Damidot	Damidot, D., Glasser, F.P., 1993. Thermodynamic investigation of the CaO-Al_2O_3-$CaSO_4$-H_2O system at 25°C and the influence of Na_2O. Cem. Concr. Res., 23, 221-238.
DWT	D.R. Turner, M. Whitfield, A.G. Dickson, 1981. The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure. Geochim. Cosmochim. Acta, 45, 855-881.
Essington	Essington, M.E., 1990. Calcium molybdate solubility in spent oil shale and a preliminary evaluation of the association constants for the formation of $CaMoO_4$(aq), $KMoO_4$(aq) and $NaMoO_4$(aq). Environ. Sci. Technol., 24, 214-220.
epri	EPRI, Fly ash and fly-ash leachate characteristics (report)
F&C	C. Fouillac, A. Criaud, 1984. Carbonate and bicarbonate trace metal complexes: Critical reevaluation of stability constants. Geochemical J., 18, 297-303.
I&N	K. Itagaki, T. Nishamura 1986. Thermodynamic properties of compounds and aqueous species of VA elements, Metall. Rev. MMIJ, 3,29-48.
Su	C. Su, 1992. Surface characteristics and thermodynamic stability of imogolite and allophane. UMI Dissertation Services, Ann Arbor, Michigan, pp. 212.
O'Hare	P.A.G. O'Hare, K.J. Jensen, H.R. Hoekstra, 1974. Thermochemistry of molybdates. IV. Standard enthalpy of formation of lithium molybdate, thermodynamic properties of the aqueous molybdate ion and thermodynamic stability of the alkali metal molybdates. J.
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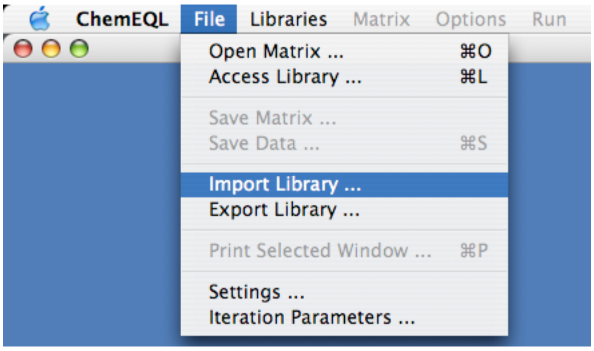
Woods&Garrels	T.L. Woods, R.M. Garrels, 1987. Thermodynamic values at low temperature for natural inorganic materials: An uncritical Summary. Oxford University Press,New York and Oxford, pp. 242.

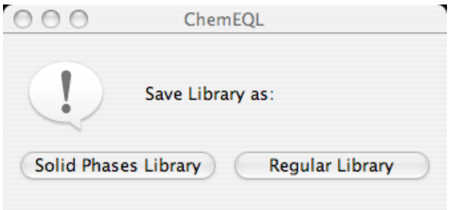
Exchange the libraries

Library files can be altered or extended and exported and exchanged with colleagues: export your library to create an EXCEL text files again with the menu command ***Export Library...***

This file format can be again imported to ChemEQL using the ***File*** menu item ***Import Library...***



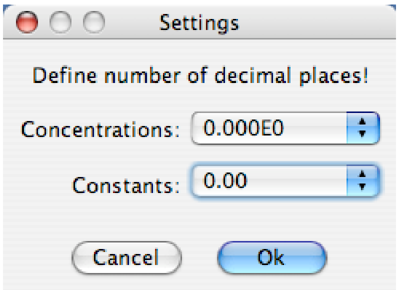
Select CQLJ.RegularLib and save it with the following window as ‘Regular Library’:



The same procedure is then repeated with the solid phase library. The imported files are automatically saved as binary files. ***Names must not be changed*** otherwise ChemEQL does not recognize the libraries and reloads the standard libraries from the ChemEQL homepage.

Settings

The ***Settings...*** window allows selection of the number of decimal places displayed in the matrix and results windows:

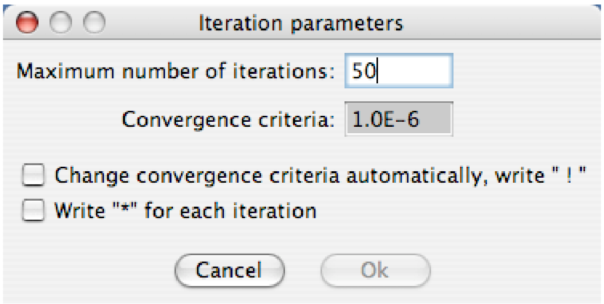


Concentrations: 0.000E0

Constants: 0.00

Iteration parameters

In case of non-convergence the calculation is stopped after 50 iterations. This number is very appropriate and does not need to be changed. In case an iteration does not converge the problem is usually an error in the matrix, see chapter ‘Iteration does not converge’.



Maximum number of iterations: 50

Convergence criteria: 1.0E-6

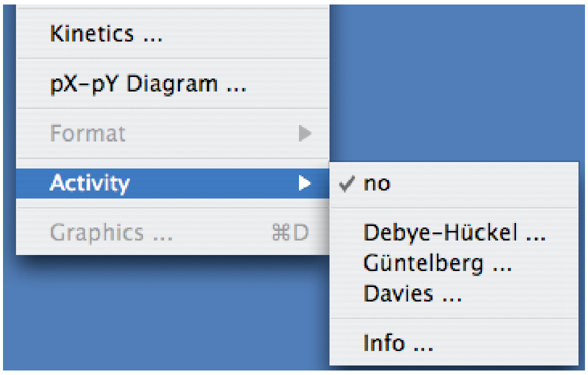
☐ Change convergence criteria automatically, write " ! "
☐ Write "*" for each iteration

For some tricky calculations of titration curves or large arrays of concentrations it may occur that an iteration error appears occasionally even though the matrix is correct, i.e. chemically sensible. Ticking the box you arrange that the convergence criteria is lowered by a factor of 10 and a **‘!’** is written to remind you that the result is questionable. The convergence criteria is setback to the original value for the following calculation automatically.

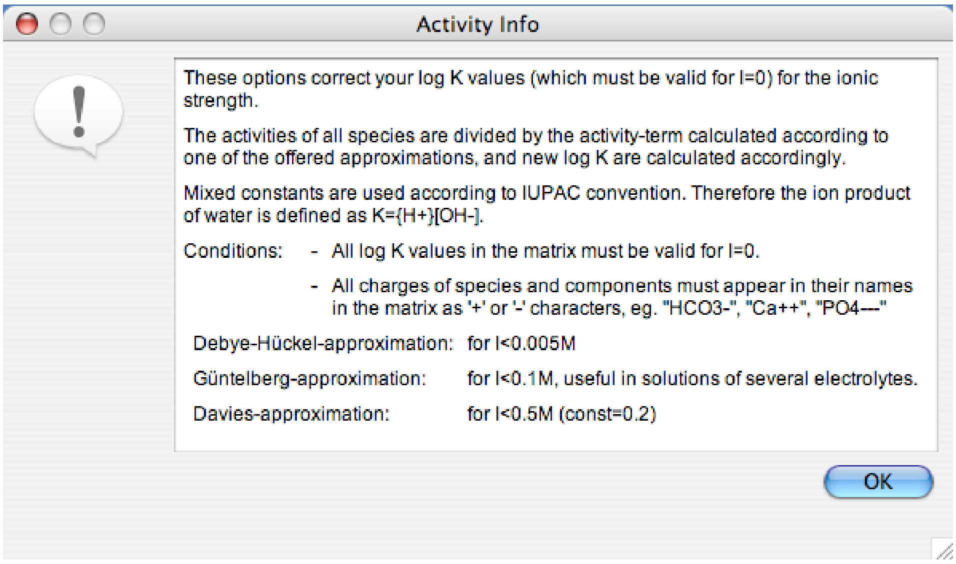
The number of iterations used in a calculation can be indicated by **‘*’** printed with the results.

Activity

Using the **Activity option** will calculate speciation in activities instead of concentrations. This is of importance particularly in solutions with high ionic strengths.



To use this option make sure that all complex formation constants are valid for an ionic strength of 0, and that charges of all components and species are included in their names as '+' or '-', e.g. 'PO4---' or 'Fe++', etc. The 'Info' window provides you with the basic knowledge for the option:



These options correct your log K values (which must be valid for I=0) for the ionic strength.

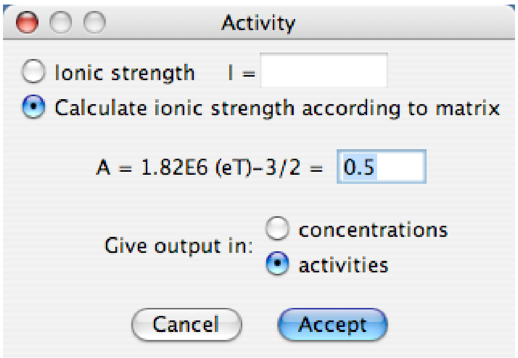
The activities of all species are divided by the activity-term calculated according to one of the offered approximations, and new log K are calculated accordingly.

Mixed constants are used according to IUPAC convention. Therefore the ion product of water is defined as K={H+}[OH-].

Conditions:
- All log K values in the matrix must be valid for I=0.
- All charges of species and components must appear in their names in the matrix as '+' or '-' characters, eg. "HCO3-", "Ca++", "PO4---"

Debye-Hückel-approximation:	for I<0.005M
Güntelberg-approximation:	for I<0.1M, useful in solutions of several electrolytes.
Davies-approximation:	for I<0.5M (const=0.2)

Choosing either ***Debye-Hückel***, ***Güntelberg*** or ***Davies*** approximation from the ***Activity*** menu will lead to the following dialog:



○ Ionic strength I =

● Calculate ionic strength according to matrix

A = 1.82E6 (eT)-3/2 = 0.5

Give output in: ○ concentrations ● activities

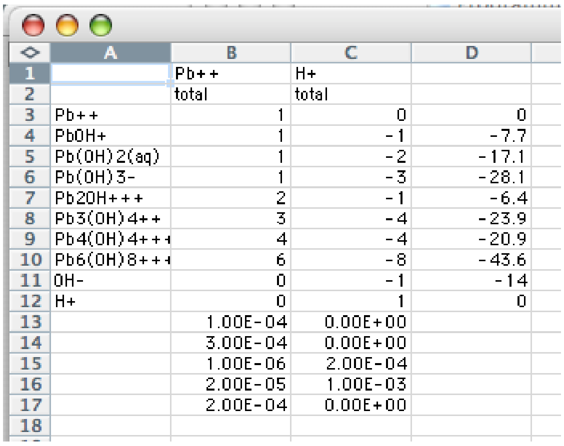
You can enter the concentration of an electrolyte that is not necessarily contained in the matrix by selecting 'Ionic strength'. The alternative choice is that you make the program calculate the ionic strength according to the species and concentrations of your matrix. The program will then include in the iterative procedure the calculation of the ionic strength with the calculated concentrations and charges found in the names of the species.

Activity coefficients are then calculated according to the selected method, and stability constants for the formation of each species corrected for the new activity coefficients. The iteration proceeds until a convergence criteria is fulfilled. If the condition cannot be satisfied after a certain number of cycles a message window will appear and the program will leave the cycle. This case usually occurs if the ionic strength is unreasonably high. (**A** is a constant used to calculate activity coefficients and is ≈0.5 in water of 25 degrees.)

Therefore the speciation calculation is performed with respect to activities. The choice between 'concentrations' and 'activities' concerns only the output values: The results can be given either in concentrations with the dimension [mol / liter], or, multiplied with the calculated activity coefficient for the respective species, in dimensionless activities. Graphics are drawn in activities. **(Activities will appear in *italic* on the datasheet)**.

Array of concentrations

A matrix can be calculated for a pH range (choose ***pH range…*** in the ***Options*** menu) or a concentration range of any component of the matrix (choose ***Component Range…*** in the ***Options*** menu. However, it can be calculated for **any arrangement of concentrations** at once (e.g. for various conditions in an experiment). In order to do this, write additional concentrations below the ‘ordinary’ concentration line of the matrix. This must be done in EXCEL, however. The program will check if there are several more concentrations to calculate or just one. The final matrix may look as follows (This matrix is in the set of examples as 'Pb.mat'):

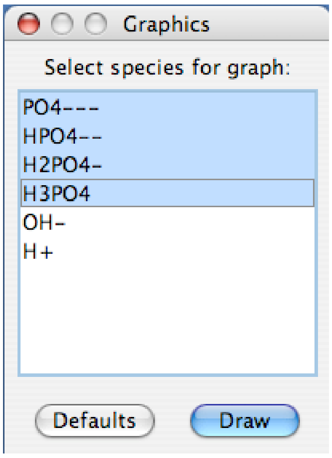


	A	B	C	D
1		Pb++	H+	
2		total	total	
3	Pb++	1	0	0
4	PbOH+	1	-1	-7.7
5	Pb(OH)2(aq)	1	-2	-17.1
6	Pb(OH)3-	1	-3	-28.1
7	Pb2OH+++	2	-1	-6.4
8	Pb3(OH)4++	3	-4	-23.9
9	Pb4(OH)4++	4	-4	-20.9
10	Pb6(OH)8++	6	-8	-43.6
11	OH-	0	-1	-14
12	H+	0	1	0
13		1.00E-04	0.00E+00	
14		3.00E-04	0.00E+00	
15		1.00E-06	2.00E-04	
16		2.00E-05	1.00E-03	
17		2.00E-04	0.00E+00	
18				

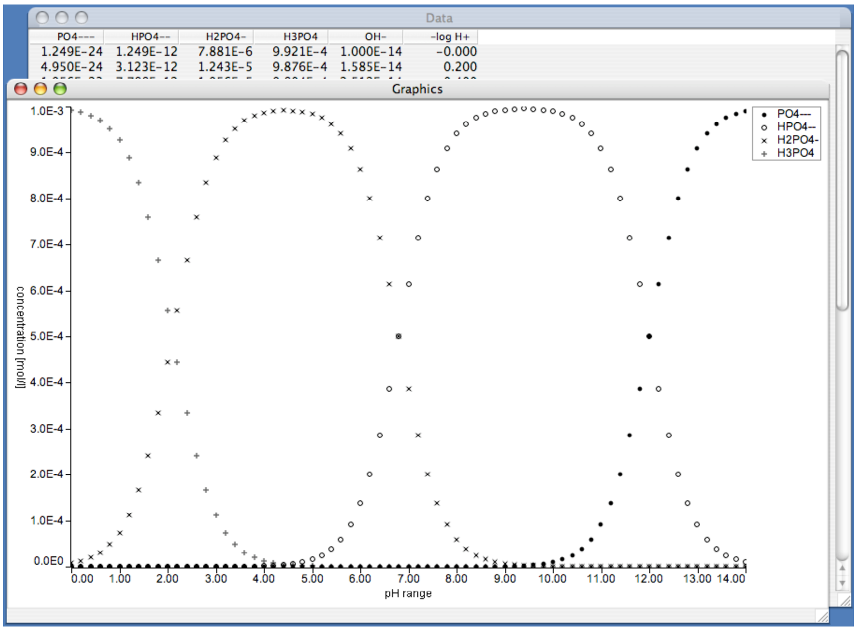
In the **current matrix** window you will find the remark, that the calculation will be performed for an **array of concentrations**.

Graphic representation

In case of calculating for an array of concentrations or a pH range you have the choice of plotting the results graphically. However, the species to be plotted must be chosen before the calculation is started. Choose ***Graphics...*** from the ***Options*** menu.



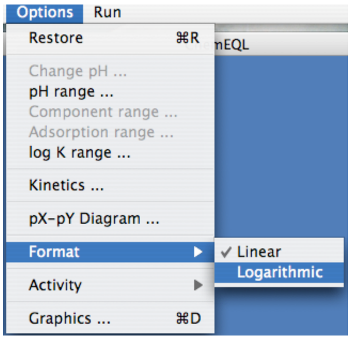
The plot window will be the front window, all data will be printed on a second window behind which can be saved after calculation:


Data

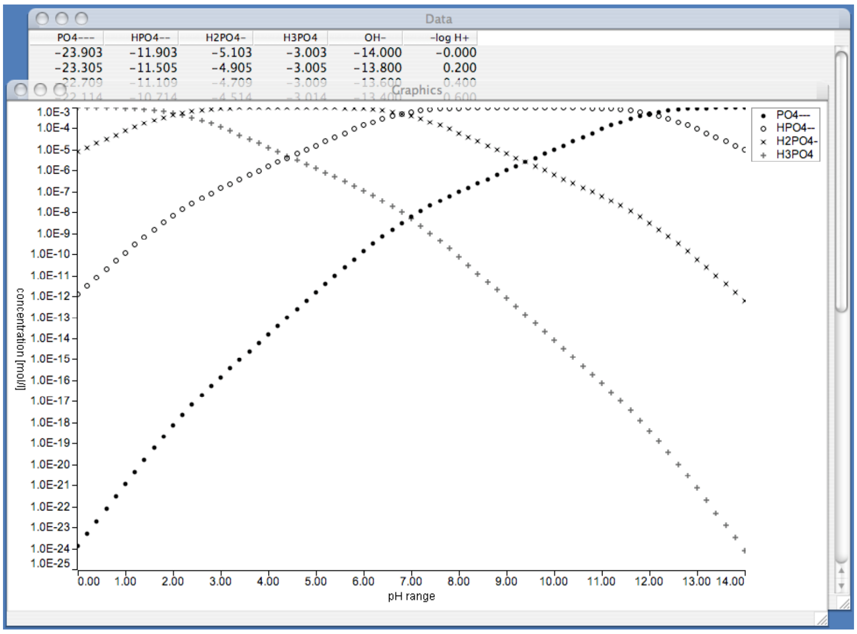
PO4---	HPO4--	H2PO4-	H3PO4	OH-	-log H+
1.249E-24	1.249E-12	7.881E-6	9.921E-4	1.000E-14	-0.000
4.950E-24	3.123E-12	1.243E-5	9.876E-4	1.585E-14	0.200

Linear / Logarithmic data format

Data output format (linear or logarithmic) can be selected from the Options menu:



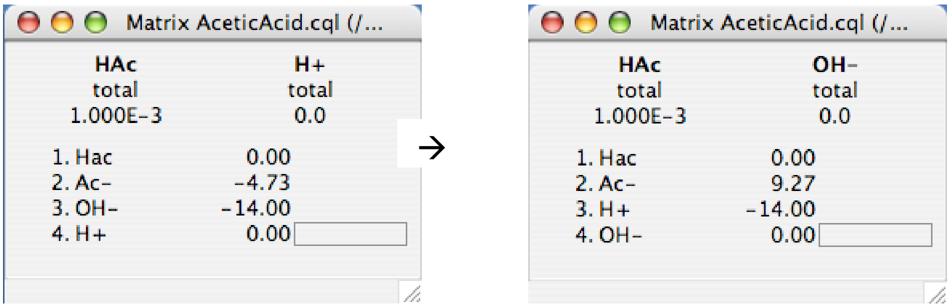
Accordingly, the data format as well as graphic plots will be given according to selection. However, the format must be selected before the calculation is started:



```
  PO4---    HPO4--    H2PO4-    H3PO4      OH-      -log H+
 -23.903   -11.903    -5.103    -3.003   -14.000    -0.000
 -23.305   -11.505    -4.905    -3.005   -13.800     0.200
 -22.709   -11.109    -4.709    -3.009   -13.600     0.400
 -22.114   -10.714    -4.514    -3.014   -13.400     0.600
```

Replace H^+ by OH^-

This is a very helpful option if instead of H^+, OH^- is needed as a component in case one wants to add OH^- to a solution or titrate an acid with a base, i.e. OH^-. Apply this command to your matrix, and all complexation constants are adjusted for OH^- instead of H^+: **The function recalculates all binding constants using the ion product of water given in the matrix.**



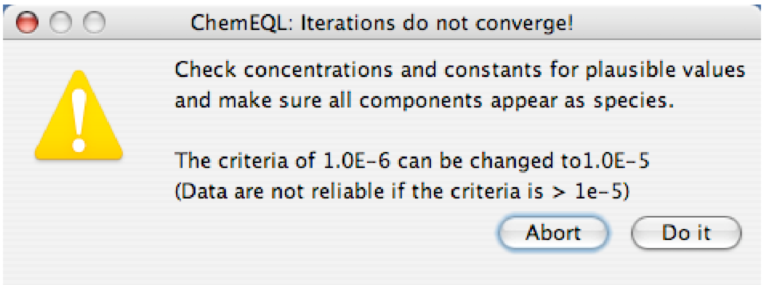
	HAc	H+
	total	total
	1.000E-3	0.0
1. Hac		0.00
2. Ac-		-4.73
3. OH-		-14.00
4. H+		0.00

	HAc	OH-
	total	total
	1.000E-3	0.0
1. Hac		0.00
2. Ac-		9.27
3. H+		-14.00
4. OH-		0.00

If OH^- is a component of the matrix, the command changes to ***'Replace OH- by H+'***.

Iteration does not converge

For some large matrixes it can occur that the calculation does not converge. However, this message usually appears if some **fundamental mistakes were made in the matrix**: The matrix does not make sense chemically, components do not appear as species, concentrations are entered as zero, stoichiometric coefficients are wrong, false binding constants lead to impossible numbers in the pursuit of the calculation etc. In this case the following window will appear:



ChemEQL: Iterations do not converge!

Check concentrations and constants for plausible values and make sure all components appear as species.

The criteria of 1.0E-6 can be changed to1.0E-5
(Data are not reliable if the criteria is > 1e-5)

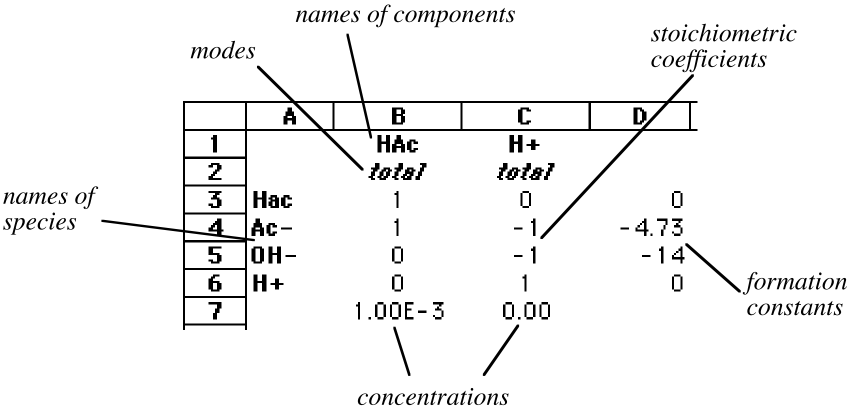
If you allow the program to be more tolerant with its convergence criteria by clicking **do it** you will find that the calculation converges immediately afterwards in case your matrix is ok. The results should be reliable. If the calculation does not converge, however, your matrix most probably contains a major mistake and the calculation it will not converge until the criteria is very large.

Never trust any data if the calculation does not converge immediately after the first warning!

How to set up a Matrix – The Details

The computer-compatible formulation of chemical reactions is designed in a matrix format. To describe the species of interest (e.g. for acetic acid: HAc, Ac^-), a minimum number of independent **components** are chosen (e.g. HAc and H^+, or Ac^- and H^+, or Ac^- and OH^-…) such that the **formation** of all **species** can be written with chemical mass action laws as the **products** of the components and binding constants. (no. of components = no. of species minus no. of independent reactions). The stoichiometric coefficients of the components whose reactions form the species of interest appear in the matrix; the **components** stand in the **columns**, the **species** in the **lines** of the matrix. The equilibrium constants are added in an additional column. The matrices must be saved as **EXCEL-text** files. The extension **'.cql'** is recognized by the program as a ChemEQL file.

A simple example of a matrix is the following:



	A	B	C	D
1		HAc	H+	
2		*total*	*total*	
3	Hac	1	0	0
4	Ac-	1	-1	-4.73
5	OH-	0	-1	-14
6	H+	0	1	0
7		1.00E-3	0.00	

Important!

- The only condition with respect to the sequence of the components is to **put H^+ in the last column and in the last line of the matrix**.
- **Each component must also appear as a species in the matrix** (with log K=0), except solid phases or surface charges.
- Write the **charges** of species and components as a number of '**+**' or '**-**' characters in the names, e.g. Pb**++**, PO_4**---** (imperative only for activity corrections).

The mode codes for the matrix:

The characterization (or **mode**) of the components which is given by the chemical question (eg. this component is a solid phase, the concentration of this component remains constant, this is a particulate surface...) is introduced in the second line of the matrix by the following codes:

Dissolved

'total'	the given concentration is the **total concentration** of this component.
'free'	the given concentration is the **free concentration** of this species that corresponds to this component and shall remain constant (eg. constant pH, equilibrium with atmospheric CO_2, free Me^{z+} constant, etc.).

Solid phases

'solidPhase'	this component is a **solid phase with activity=1**.
'checkPrecip'	to **check if this component precipitates** for a given concentration under the chosen conditions, or define the amount of a solid phase that can be dissolved.

Adsorption

ConstantCap, Diffuse/GTL, SternL, and TripleL (Model of choice, see examples).

'adsorbent1', 'adsorbent2', ... 'adsorbent5' indicate different types of particles.

Several types of surface sites for one particle type (up to three are possible) are named:

'adsorbent1.1', 'adsorbent1.2' ..., the numbers meaning (*which particle.which site*).

The charges have to be named

'charge1.1' ... 'charge5.1' (for *ConstantCap* and *Diffuse/GTL*),

'charge1.1' 'charge1.2' ... 'charge5.1' 'charge5.2' (for *SternL*), and

'charge1.1' 'charge1.2', **'charge1.3' ... 'charge5.1' 'charge5.2'**, **'charge5.3'** (for *TripleL*). The numbers mean (*which particle.which charge*)

Creating a matrix by hand

Assume you want to calculate the pH and the distribution of the protonated and deprotonated species of a 10^{-3} molar solution of acetic acid in pure water:

1st List all chemical **species** that occur in the system:

HAc, Ac^-, OH^- and **H^+**

2nd Look for a minimum amount of **components** with which you are able to formulate the chemical formation of all your species (you need the chemical equilibrium formation constants, e.g. from Martell and Smith, Critical Stability Constants, 1974-82). In our example this can be **HAc and H^+**. (Alternatively, the formation of the above species can be described with HAc and OH^-, with Ac^- and H^+, or Ac^- and OH^-).

3rd Write chemical equations for the **formation** of species using only components:

formation of HAc:	HAc	⇔	**HAc**	$\log K_1 = 0$
formation of Ac^-:	HAc	⇔	**Ac^-** + H^+	$\log K_2 = -4.73$
formation of OH^-:	H_2O	⇔	**OH^-** + H^+	$\log K_3 = -14$
formation of H^+:	H^+	⇔	**H^+**	$\log K_4 = 0$

4th Write mass action expression for the species according to the above equations:

$$HAc = K_1 \cdot HAc^{\mathbf{1}}$$

$$Ac^- = K_2 \cdot HAc^{\mathbf{1}} \cdot [H^+]^{\mathbf{-1}}$$

$$OH^- = K_3 \cdot [H^+]^{\mathbf{1}}$$

$$H^+ = K_4 \cdot [H^+]^{\mathbf{1}}$$

5th The above equations define the system completely. To read these equations with a computer program, we put the stoichiometric coefficients, which are the exponents of the above equations, into a matrix of the following setup: species form the lines, components the columns. Formation constants are added to the line of the corresponding species:

	HAc	**H^+**	*{log K}*
Hac	1	0	0
Ac^-	1	-1	-4.73
OH^-	0	-1	-14
H^+	0	1	0

6th The concentrations of the components are added at the end of the columns. We start out with 10^{-3} moles of HAc in one liter of pure water (no strong acid added, therefore the start total concentration of H^+=0). Calculation for a variety of concentrations is possible by just adding the next concentrations in the subsequent lines (see example A).

Since the program needs to know the meaning of the concentration of the components (e.g. are these total concentrations, or is one of them the concentration of the free species, or is one of the components a solid phase or an adsorbing surface etc.) we have to define the *mode* of each component. In our case the concentration of HAc is the *total* amount that is in the system and such is H^+. (In case you want to give the pH however, you have to give the concentration of the *free* species H^+ (which is measured as pH).)

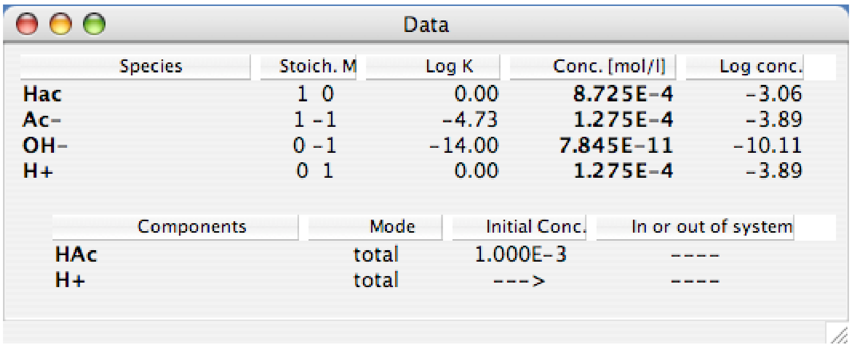
A collection of all predefined codes was given above. For our example they are '**total**' for both HAc and H^+. They are added underneath the component names. Modes are fixed codes that are recognized by the program. Names of species and components can be anything (or nothing); it's just a text, except **'H+'** in the last column so the program knows it's the pH.

The program needs to know the **charges** of the species and components (only in case activity coefficients and thus **ionic strength** is calculated). Write charges as '**+**' or '**-**' characters, e.g. Pb**++**, PO4**---**, etc.

This is the final format for our matrix! Remarks or information about the stability constants can be added to the right of the stability constants in {parenthesis}. Write on an **EXCEL** spreadsheet and save it in **text** format. The extension '.cql' is recognized by the program as a chemical matrix. (The following matrix is in your set of examples in the 'demo' folder and is called '*aceticAcid.mat*'

	HAc **total**	**H^+** **total**	*{log K}*	
Hac	1	0	0	
Ac^-	1	-1	-4.73	{25 deg, I=0}
OH^-	0	-1	-14	
H^+	0	1	0	
	10^{-3}	**0**		

Start the program, read the matrix by choosing ***Open Matrix...*** from the ***File*** menu, and start the calculation with ***Go*** in the ***Run*** menu. You will obtain the following output:



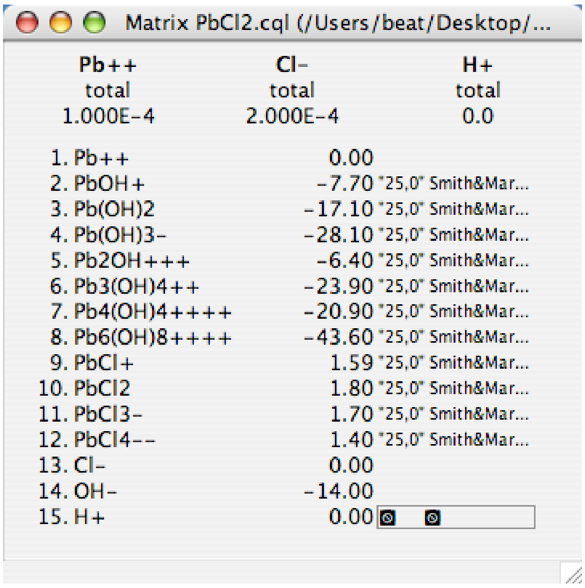
```
Species            Stoich. M   Log K    Conc. [mol/l]   Log conc.
Hac                  1  0       0.00     8.725E-4        -3.06
Ac-                  1 -1      -4.73     1.275E-4        -3.89
OH-                  0 -1     -14.00     7.845E-11      -10.11
H+                   0  1       0.00     1.275E-4        -3.89

   Components           Mode    Initial Conc.   In or out of system
   HAc                  total   1.000E-3             ----
   H+                   total   --->                 ----
```

Data can be saved with ***Save Data...*** (recommended extension: **.xls**) and the matrix file with ***Save Matrix...*** (recommended extension **.cql**) under the ***File*** menu.

Regular species distribution in homogeneous solution

The simplest case for a speciation calculation is a system where all components are dissolved, and total concentrations are known: ***A solution of 10^{-4} moles/l of $PbCl_2$ in pure water.***

Pb++, Cl- and **H+** are selected for components. The combination of these three components describes the formation of all species. (Of course one can choose other components as well, such as PbOH+ and OH- if you wish for some reason). The components are selected from the library, with the corresponding concentrations. The matrix looks as follows:

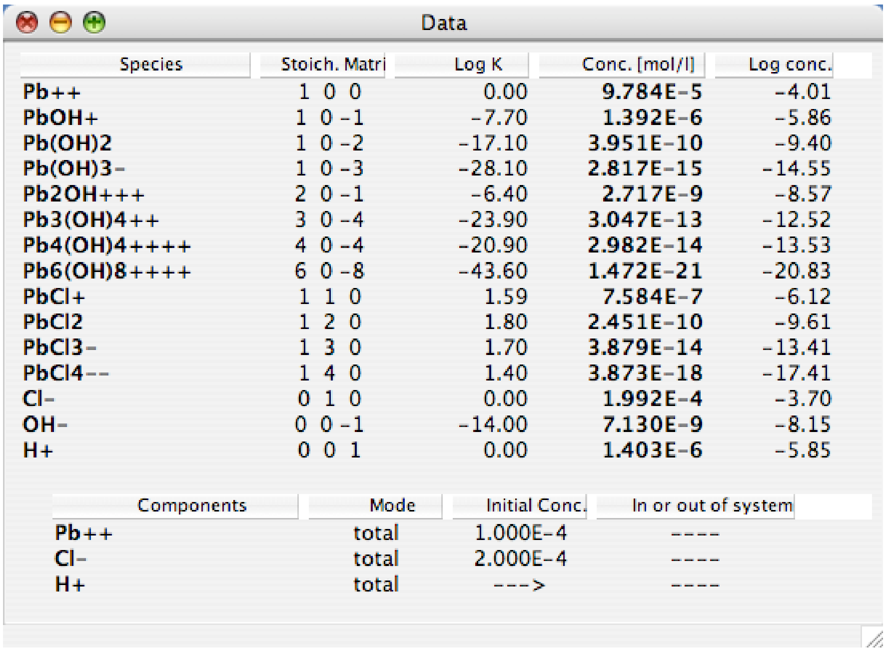


Pb++	Cl-	H+
total	total	total
1.000E-4	2.000E-4	0.0

1. Pb++	0.00	
2. PbOH+	-7.70	"25,0" Smith&Mar...
3. Pb(OH)2	-17.10	"25,0" Smith&Mar...
4. Pb(OH)3-	-28.10	"25,0" Smith&Mar...
5. Pb2OH+++	-6.40	"25,0" Smith&Mar...
6. Pb3(OH)4++	-23.90	"25,0" Smith&Mar...
7. Pb4(OH)4++++	-20.90	"25,0" Smith&Mar...
8. Pb6(OH)8++++	-43.60	"25,0" Smith&Mar...
9. PbCl+	1.59	"25,0" Smith&Mar...
10. PbCl2	1.80	"25,0" Smith&Mar...
11. PbCl3-	1.70	"25,0" Smith&Mar...
12. PbCl4--	1.40	"25,0" Smith&Mar...
13. Cl-	0.00	
14. OH-	-14.00	
15. H+	0.00	

This matrix is in the demo folder and called 'PbCl2.mat'. The remarks to the right of the complex formation constants give information on the conditions and origin of the constants: The first number indicates the **temperature** and the second number the **ionic strength** at which the constants were determined. Binding constants are from **Smith&Martell**: Smith and Martell, Critical Stability Constants (1976).

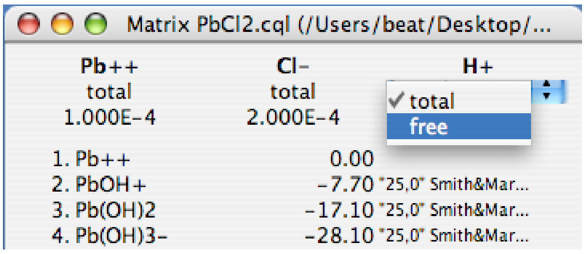
Go from the Run menu produces the following datasheet. You find that pH of the solution is 5.85, and that chloro complexes are negligible:



Species	Stoich. Matri	Log K	Conc. [mol/l]	Log conc.
Pb++	1 0 0	0.00	**9.784E-5**	-4.01
PbOH+	1 0 -1	-7.70	**1.392E-6**	-5.86
Pb(OH)2	1 0 -2	-17.10	**3.951E-10**	-9.40
Pb(OH)3-	1 0 -3	-28.10	**2.817E-15**	-14.55
Pb2OH+++	2 0 -1	-6.40	**2.717E-9**	-8.57
Pb3(OH)4++	3 0 -4	-23.90	**3.047E-13**	-12.52
Pb4(OH)4++++	4 0 -4	-20.90	**2.982E-14**	-13.53
Pb6(OH)8++++	6 0 -8	-43.60	**1.472E-21**	-20.83
PbCl+	1 1 0	1.59	**7.584E-7**	-6.12
PbCl2	1 2 0	1.80	**2.451E-10**	-9.61
PbCl3-	1 3 0	1.70	**3.879E-14**	-13.41
PbCl4--	1 4 0	1.40	**3.873E-18**	-17.41
Cl-	0 1 0	0.00	**1.992E-4**	-3.70
OH-	0 0 -1	-14.00	**7.130E-9**	-8.15
H+	0 0 1	0.00	**1.403E-6**	-5.85

Components	Mode	Initial Conc.	In or out of system
Pb++	total	1.000E-4	----
Cl-	total	2.000E-4	----
H+	total	--->	----

You might want to calculate a speciation for a constant pH. In that case you must change the **'mode'** of the **'H+'** component from **'total'** to '**free**' since you want the free concentration of H^+ to be a certain value. Click in the mode code in the matrix window will produce a pop up menu that lets you change the mode:

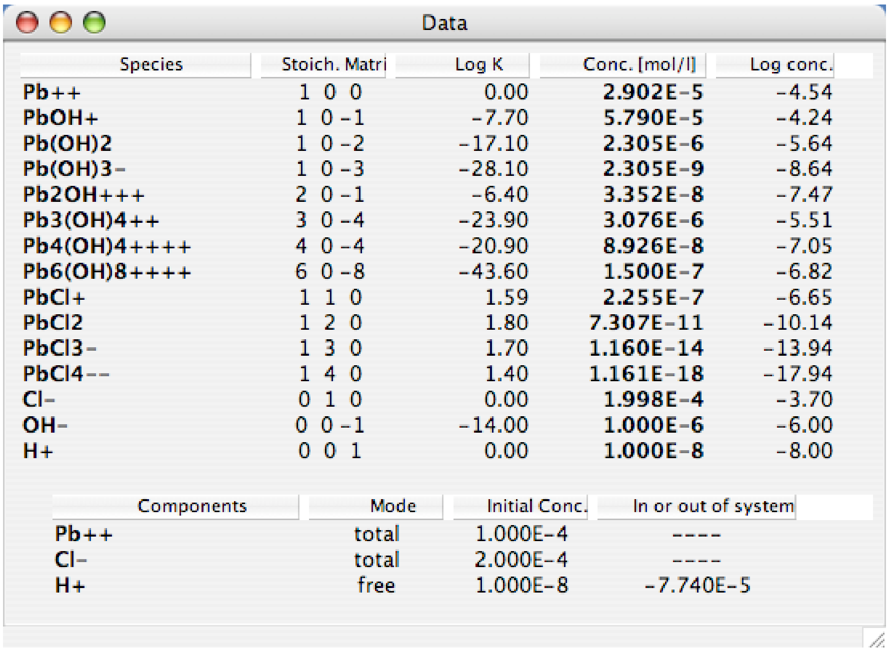


Pb++	Cl-	H+
total	total	total
1.000E-4	2.000E-4	

1. Pb++ 0.00
2. PbOH+ -7.70 "25,0" Smith&Mar...
3. Pb(OH)2 -17.10 "25,0" Smith&Mar...
4. Pb(OH)3- -28.10 "25,0" Smith&Mar...

To change the concentration of H^+ just enter '1e-8' in the number field in the interactive matrix window.

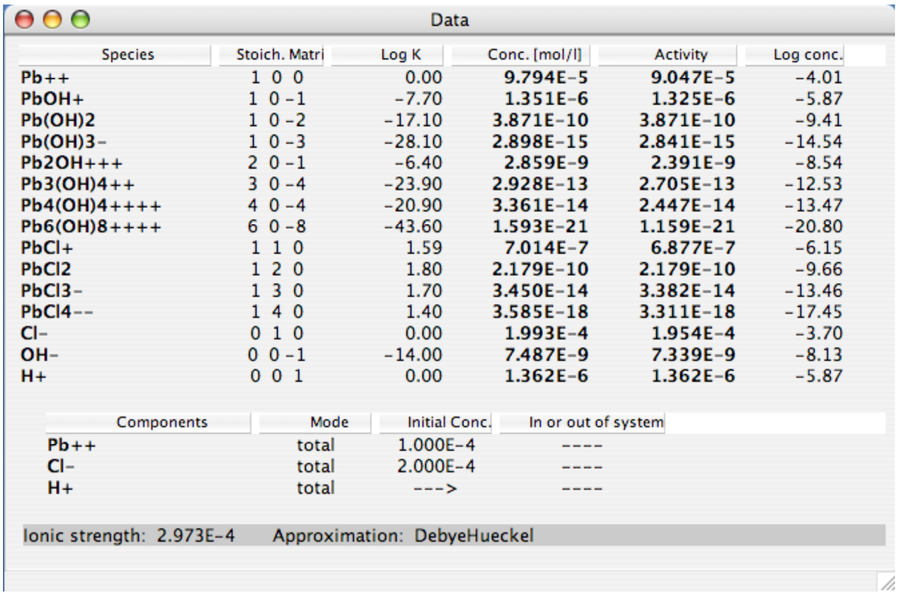
Go will calculate the speciation of the system with 10^{-4} moles of $PbCl_2$ in 1 liter of water at a pH of 8. Note that you had to remove $7.74 \cdot 10^{-5}$ moles of H^+ from that system in order to sustain a pH of 8:



Species	Stoich. Matri	Log K	Conc. [mol/l]	Log conc.
Pb++	1 0 0	0.00	2.902E-5	-4.54
PbOH+	1 0 -1	-7.70	5.790E-5	-4.24
Pb(OH)2	1 0 -2	-17.10	2.305E-6	-5.64
Pb(OH)3-	1 0 -3	-28.10	2.305E-9	-8.64
Pb2OH+++	2 0 -1	-6.40	3.352E-8	-7.47
Pb3(OH)4++	3 0 -4	-23.90	3.076E-6	-5.51
Pb4(OH)4++++	4 0 -4	-20.90	8.926E-8	-7.05
Pb6(OH)8++++	6 0 -8	-43.60	1.500E-7	-6.82
PbCl+	1 1 0	1.59	2.255E-7	-6.65
PbCl2	1 2 0	1.80	7.307E-11	-10.14
PbCl3-	1 3 0	1.70	1.160E-14	-13.94
PbCl4--	1 4 0	1.40	1.161E-18	-17.94
Cl-	0 1 0	0.00	1.998E-4	-3.70
OH-	0 0 -1	-14.00	1.000E-6	-6.00
H+	0 0 1	0.00	1.000E-8	-8.00

Components	Mode	Initial Conc.	In or out of system
Pb++	total	1.000E-4	----
Cl-	total	2.000E-4	----
H+	free	1.000E-8	-7.740E-5

With ***Activity…*** binding constants are corrected for ionic strength either with Debye-Hückel, Güntelberg, or Davies approximation. It is imperative that binding constants in the matrix are valid for I=0 and that charges of all components and species are present as '+' and '-' characters. There is the option to define a ionic strength or let the program calculate the ionic strength that results from the concentration input data of your matrix (for more information see section 'Activity'). For our system with 10^{-4} mol/l $PbCl_2$ the data sheet will give both concentrations and activities. Differences between concentrations and activities in this system are very small:

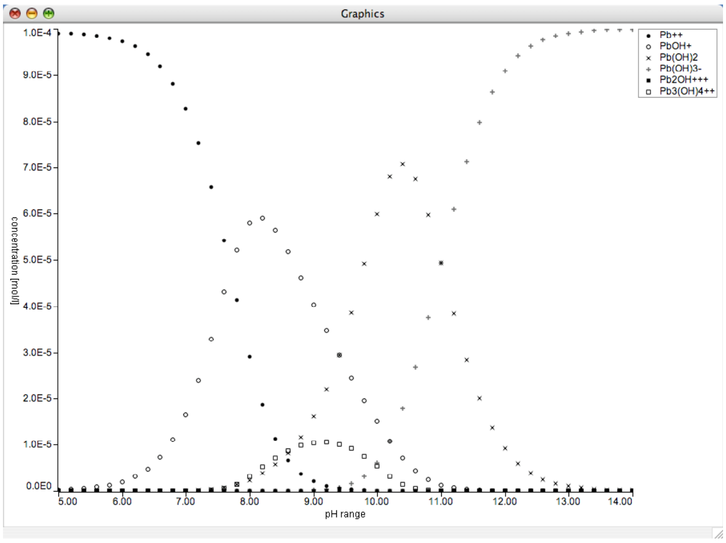


Species	Stoich. Matri	Log K	Conc. [mol/l]	Activity	Log conc.
Pb++	1 0 0	0.00	**9.794E-5**	**9.047E-5**	-4.01
PbOH+	1 0 -1	-7.70	**1.351E-6**	**1.325E-6**	-5.87
Pb(OH)2	1 0 -2	-17.10	**3.871E-10**	**3.871E-10**	-9.41
Pb(OH)3-	1 0 -3	-28.10	**2.898E-15**	**2.841E-15**	-14.54
Pb2OH+++	2 0 -1	-6.40	**2.859E-9**	**2.391E-9**	-8.54
Pb3(OH)4++	3 0 -4	-23.90	**2.928E-13**	**2.705E-13**	-12.53
Pb4(OH)4++++	4 0 -4	-20.90	**3.361E-14**	**2.447E-14**	-13.47
Pb6(OH)8++++	6 0 -8	-43.60	**1.593E-21**	**1.159E-21**	-20.80
PbCl+	1 1 0	1.59	**7.014E-7**	**6.877E-7**	-6.15
PbCl2	1 2 0	1.80	**2.179E-10**	**2.179E-10**	-9.66
PbCl3-	1 3 0	1.70	**3.450E-14**	**3.382E-14**	-13.46
PbCl4--	1 4 0	1.40	**3.585E-18**	**3.311E-18**	-17.45
Cl-	0 1 0	0.00	**1.993E-4**	**1.954E-4**	-3.70
OH-	0 0 -1	-14.00	**7.487E-9**	**7.339E-9**	-8.13
H+	0 0 1	0.00	**1.362E-6**	**1.362E-6**	-5.87

Components	Mode	Initial Conc.	In or out of system
Pb++	total	1.000E-4	----
Cl-	total	2.000E-4	----
H+	total	--->	----

Ionic strength: 2.973E-4 Approximation: DebyeHueckel

In order to display the pattern of Pb species in a pH range choose ***pH range...*** from the ***Option*** menu and enter the range of interest in reasonable steps, e.g. from 5 to 14 in steps of 0.25 pH units. Represent the curves graphically for better overview by choosing ***Graphics...*** from the ***Options*** menu and select the species of interest. This will produce the following output:



A datasheet that can be saved is printed in the back of the plot.

Octanol-water and gas-water distribution

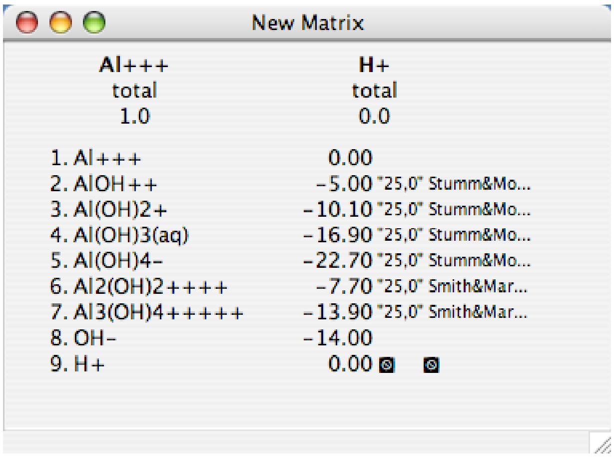
Equilibrium calculations that contain **octanol-water distribution**, **gas-water (Henry) coefficients** or dissolution of organic substances can easily be included in speciation calculations. Use the octanol-water or Henry coefficients in the same way as regular formation constants are used to characterize the species.

Solid phases: dissolution and precipitation

Put up a matrix to calculate solubility

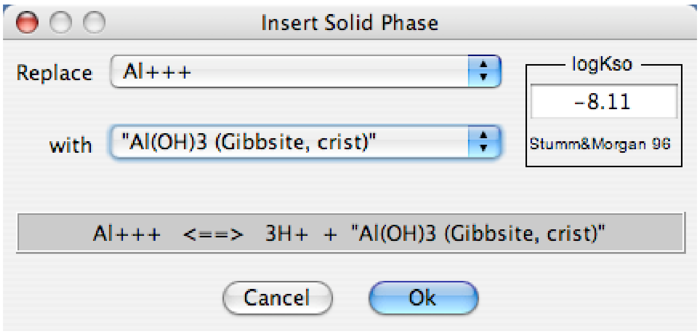
We use the dissolution of Al(OH)$_3$(Gibbsite) as an example to demonstrate the calculation when **one (or more) component(s) is a solid phase:**

Al-species must be described using the solubility product of the solid phase, Al(OH)$_3$(Gibbsite). Collect **'Al+++'** and **'H+'** from the Regular Library (***Access Library...***):



```
          Al+++                      H+
          total                      total
           1.0                        0.0

   1. Al+++                        0.00
   2. AlOH++                      -5.00 "25,0" Stumm&Mo...
   3. Al(OH)2+                   -10.10 "25,0" Stumm&Mo...
   4. Al(OH)3(aq)                -16.90 "25,0" Stumm&Mo...
   5. Al(OH)4-                   -22.70 "25,0" Stumm&Mo...
   6. Al2(OH)2++++                -7.70 "25,0" Smith&Mar...
   7. Al3(OH)4+++++              -13.90 "25,0" Smith&Mar...
   8. OH-                        -14.00
   9. H+                           0.00
```

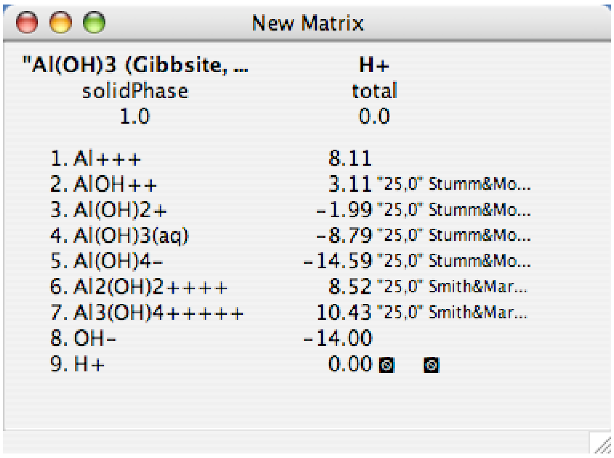
Then insert **'Al(OH)3(Gibbsite)'** to replace 'Al+++' (***Insert Solid Phase...***):



Replace: Al+++
with: "Al(OH)3 (Gibbsite, crist)"
logKso: -8.11
Stumm&Morgan 96

Al+++ <==> 3H+ + "Al(OH)3 (Gibbsite, crist)"

The equation for which the solubility product is valid is shown in the gray text field. Replacement can be performed only if the matrix contains all components that occur in this equation (an error message will occur if this is not the case). The active text field allows you to enter your own solubility constant if you do not want to use the one given by the library. If the setting is correct the program will introduce the solid phase in the matrix, recalculate all stoichiometric coefficients and binding constants, set the mode to 'solidPhase' and the activity = 1:

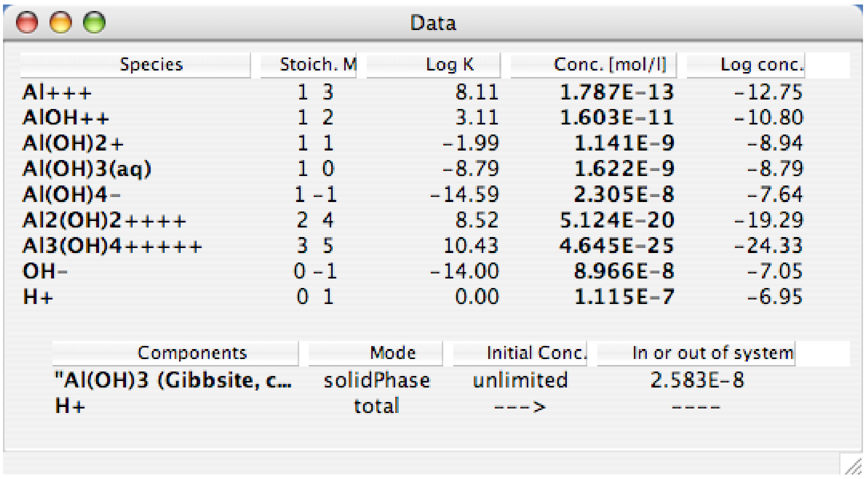


```
"Al(OH)3 (Gibbsite, ...          H+
       solidPhase              total
          1.0                   0.0

   1. Al+++                     8.11
   2. AlOH++                    3.11 "25,0" Stumm&Mo...
   3. Al(OH)2+                 -1.99 "25,0" Stumm&Mo...
   4. Al(OH)3(aq)              -8.79 "25,0" Stumm&Mo...
   5. Al(OH)4-                -14.59 "25,0" Stumm&Mo...
   6. Al2(OH)2++++              8.52 "25,0" Smith&Mar...
   7. Al3(OH)4+++++            10.43 "25,0" Smith&Mar...
   8. OH-                     -14.00
   9. H+                        0.00
```

(This matrix is stored in the ‘demo’ folder as 'Al(OH)3.cql')

Dissolution

The above matrix characterizes the dissolution of a chunk of Gibbsite in pure water (without CO_2). Calculation will result in the composition of the solution in thermodynamic equilibrium and the amount of Gibbsite dissolved ($2.58 \cdot 10^{-8}$ mol/l):

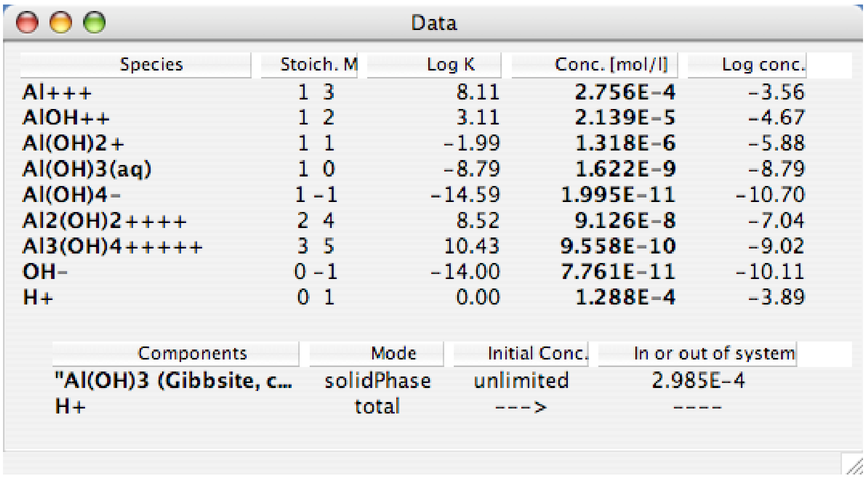


Species	Stoich. M	Log K	Conc. [mol/l]	Log conc.
Al+++	1 3	8.11	1.787E-13	-12.75
AlOH++	1 2	3.11	1.603E-11	-10.80
Al(OH)2+	1 1	-1.99	1.141E-9	-8.94
Al(OH)3(aq)	1 0	-8.79	1.622E-9	-8.79
Al(OH)4-	1 -1	-14.59	2.305E-8	-7.64
Al2(OH)2++++	2 4	8.52	5.124E-20	-19.29
Al3(OH)4+++++	3 5	10.43	4.645E-25	-24.33
OH-	0 -1	-14.00	8.966E-8	-7.05
H+	0 1	0.00	1.115E-7	-6.95

Components	Mode	Initial Conc.	In or out of system
"Al(OH)3 (Gibbsite, c...	solidPhase	unlimited	2.583E-8
H+	total	--->	----

Dissolution in acidic solution

Of course you can dissolve a lot more Gibbsite when the solution is acidified. Lets add, say 10^{-3} moles of strong acid: change the concentration of **'H+'** in the interactive matrix window, but leave the mode **'total'**. Then start the calculation. We end up with a solution of pH about 3.9 and $2.985 \cdot 10^{-4}$ moles $Al(OH)_3$(Gibbsite) dissolved:

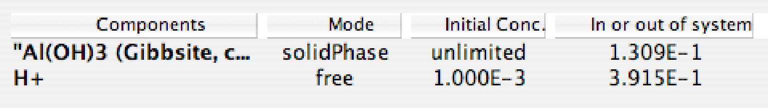


Species	Stoich. M	Log K	Conc. [mol/l]	Log conc.
Al+++	1 3	8.11	2.756E-4	-3.56
AlOH++	1 2	3.11	2.139E-5	-4.67
Al(OH)2+	1 1	-1.99	1.318E-6	-5.88
Al(OH)3(aq)	1 0	-8.79	1.622E-9	-8.79
Al(OH)4-	1 -1	-14.59	1.995E-11	-10.70
Al2(OH)2++++	2 4	8.52	9.126E-8	-7.04
Al3(OH)4+++++	3 5	10.43	9.558E-10	-9.02
OH-	0 -1	-14.00	7.761E-11	-10.11
H+	0 1	0.00	1.288E-4	-3.89

Components	Mode	Initial Conc.	In or out of system
"Al(OH)3 (Gibbsite, c...	solidPhase	unlimited	2.985E-4
H+	total	--->	----

Dissolution at constant pH

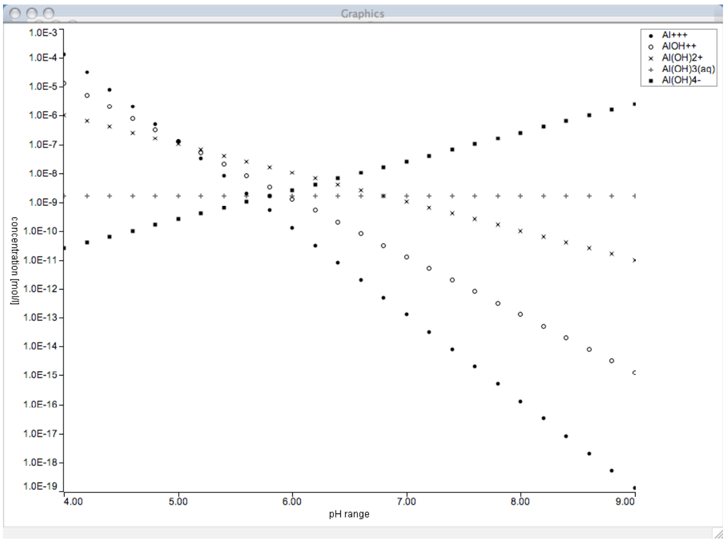
Changing the mode from **'total'** to **'free'** indicates a system where pH is held constant at pH = 3. The result sheet shows that 0.13 mol Gibbsite was dissolved in one liter, and that 0.39 mol H^+ was needed per liter to keep the pH constant at 3.0:



Components	Mode	Initial Conc.	In or out of system
"Al(OH)3 (Gibbsite, c...	solidPhase	unlimited	1.309E-1
H+	free	1.000E-3	3.915E-1

Graphical representation of solubility over a pH range

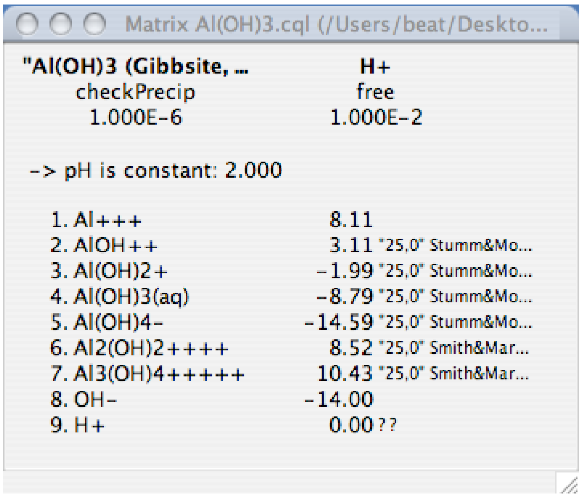
Calculate the solubility of Gibbsite in the natural pH range of water and display the result logarithmically versus pH (log-log plot): Change the ***mode*** of 'H+' from ***'total'*** to ***'free'*** with the pop up menu in the matrix window. Then choose a ***pH range...*** (***Options*** menu) from 3 to 8 in steps of 0.2. Select ***Graphics...*** (***Options*** menu) and mark the first 5 Al-species. Finally, change the ***Format*** (Options menu) from ***'Linear'*** to ***'Logarithmic'***. ***Go*** in the ***Run*** menu will produce the following plot:



Precipitation

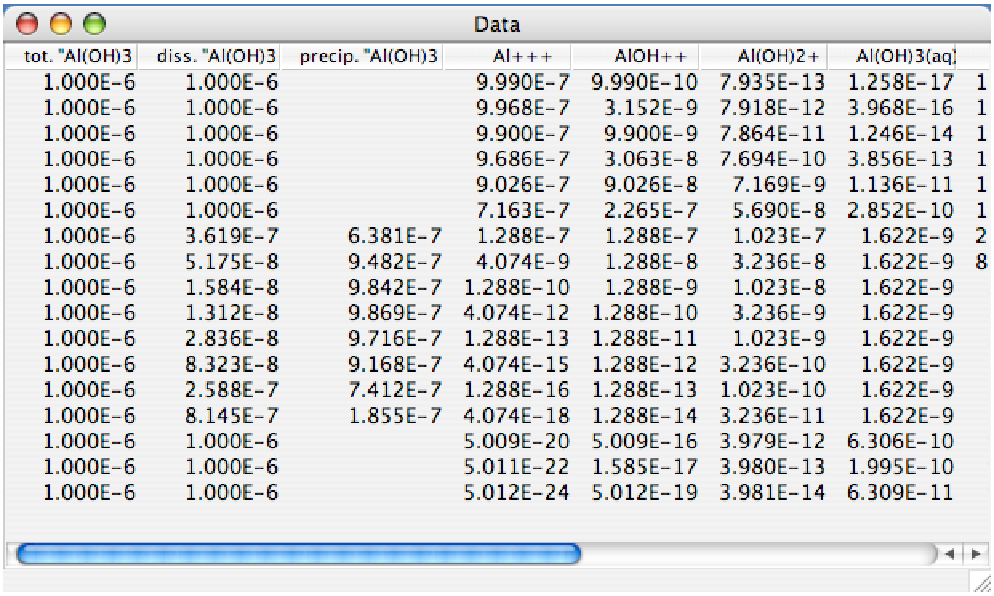
The code **'checkPrecip'** allows to test if a solution of given composition is oversaturated or undersaturated with respect to a solid phase. For an example, we start with a solution of 10^{-6} moles of Gibbsite in a solution of pH 2 and want to know when Gibbsite precipitates (if at all) if we rise the pH continuously, e.g. during a titration.

This task can be accomplished with the same matrix. Change the mode code of 'Al(OH)$_3$(Gibbsite)' from '**solidPhase**' to '**checkPrecip**'. The component now stands for *total Al in the system* and requires a concentration. Enter **'1e-6'**. Adjust the concentration of **'H+'** to **'1e-2'** and make sure the mode is **'free'**, indicating constant pH. The matrix now looks like this:



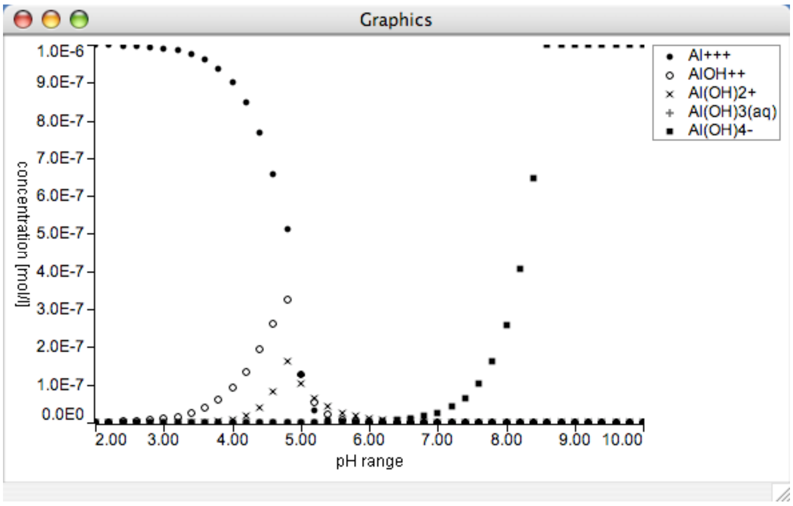
```
"Al(OH)3 (Gibbsite, ...          H+
     checkPrecip                 free
       1.000E-6                1.000E-2

 -> pH is constant: 2.000

   1. Al+++                      8.11
   2. AlOH++                     3.11 "25,0" Stumm&Mo...
   3. Al(OH)2+                  -1.99 "25,0" Stumm&Mo...
   4. Al(OH)3(aq)               -8.79 "25,0" Stumm&Mo...
   5. Al(OH)4-                 -14.59 "25,0" Stumm&Mo...
   6. Al2(OH)2++++               8.52 "25,0" Smith&Mar...
   7. Al3(OH)4+++++             10.43 "25,0" Smith&Mar...
   8. OH-                      -14.00
   9. H+                         0.00 ??
```

To check for the pH region where precipitation possibly occurs choose a pH region, eg from 2 to 10 in steps of 0.5 (***pH range...*** in the ***Option*** menu), then ***Go***. You will get the following datasheet:



tot. "Al(OH)3	diss. "Al(OH)3	precip. "Al(OH)3	Al+++	AlOH++	Al(OH)2+	Al(OH)3(aq)	
1.000E-6	1.000E-6		9.990E-7	9.990E-10	7.935E-13	1.258E-17	1
1.000E-6	1.000E-6		9.968E-7	3.152E-9	7.918E-12	3.968E-16	1
1.000E-6	1.000E-6		9.900E-7	9.900E-9	7.864E-11	1.246E-14	1
1.000E-6	1.000E-6		9.686E-7	3.063E-8	7.694E-10	3.856E-13	1
1.000E-6	1.000E-6		9.026E-7	9.026E-8	7.169E-9	1.136E-11	1
1.000E-6	1.000E-6		7.163E-7	2.265E-7	5.690E-8	2.852E-10	1
1.000E-6	3.619E-7	6.381E-7	1.288E-7	1.288E-7	1.023E-7	1.622E-9	2
1.000E-6	5.175E-8	9.482E-7	4.074E-9	1.288E-8	3.236E-8	1.622E-9	8
1.000E-6	1.584E-8	9.842E-7	1.288E-10	1.288E-9	1.023E-8	1.622E-9	
1.000E-6	1.312E-8	9.869E-7	4.074E-12	1.288E-10	3.236E-9	1.622E-9	
1.000E-6	2.836E-8	9.716E-7	1.288E-13	1.288E-11	1.023E-9	1.622E-9	
1.000E-6	8.323E-8	9.168E-7	4.074E-15	1.288E-12	3.236E-10	1.622E-9	
1.000E-6	2.588E-7	7.412E-7	1.288E-16	1.288E-13	1.023E-10	1.622E-9	
1.000E-6	8.145E-7	1.855E-7	4.074E-18	1.288E-14	3.236E-11	1.622E-9	
1.000E-6	1.000E-6		5.009E-20	5.009E-16	3.979E-12	6.306E-10	
1.000E-6	1.000E-6		5.011E-22	1.585E-17	3.980E-13	1.995E-10	
1.000E-6	1.000E-6		5.012E-24	5.012E-19	3.981E-14	6.309E-11	

The first column of the datasheet gives the total concentration (the sum of dissolved and precipitated Al), the second column the total amount of actual dissolved Al. The third column lists the amount of Gibbsite precipitated from the solution – which is the difference between total and dissolved Al. All following columns express species concentrations as usual. Each line is the result of the calculation for a given pH. Graphically displayed:



Adsorption to particulate surfaces

Introduction to the principles of surface adsorption

This chapter gives a short introduction of the ideas of adsorption models, the information needed to implement the various electrostatic models in *ChemEQL*, and how to include the specific surface parameters in the matrix. For detailed discussion of the models as well as good reviews see Dzombak and Morel (1990), J. Westall and H. Hohl (1980), or Stumm and Morgan (1996).

The free energy of adsorption actually consists of a **chemical term** describing the chemical interactions, and an **electrostatic term** accounting for electrostatic attraction and repulsion that occur at interfaces:

$$\Delta G = \Delta G_{chemical} + \Delta G_{electrostatic}$$

The electrostatic term can be looked at as a type of activity coefficient that has to be taken into account for adsorption reactions of charged species. The coulombic term expresses the work needed to transport n charges through a potential gradient Ψ:

$$\Delta G_{electrostatic} = nF\Psi$$

where F the Faraday constant (electrical charge of 1 mole of electrons) and Ψ the surface potential in Volts. Since $\Delta G_{chemical} = -RT \ln K$ we can write adsorption reaction constants as

$$K = K_{int} \cdot \exp(-nF\Psi/RT)$$

R is the molar gas constant and T the absolute temperature. The exponential term is compatible with the chemical potential term and can therefore be included in the set of components. The formation of adsorbed species can now be described by introducing their charge in the column with the exponential term in addition to the chemical interaction. The concentration that is to put for this column is the total sum of all surface charges:

$$P_{tot} = (\{\equiv SOH_2^+\} + \{\equiv SOPb^+\} + \ldots) - (\{\equiv SO^-\} + \ldots)$$

or expressed as a charge: $\sigma = P_{tot} \cdot F/SA$

where S is the specific surface area, and A the concentration of solid.

Different relationships between charge and surface potential can be thought of and therefore various models were created accordingly, the most simple one being the constant capacitance model where charge and potential are related only through the capacitance C (see literature cited above):

$$\sigma = C \cdot \Psi$$

The recent literature recommends to use the model of the Diffuse Double Layer (Dzombak and Morel, 1990; Stumm, 1997) where

$$s = (8RT\varepsilon\varepsilon_0 c \cdot 10^3)^{1/2} \sinh\left(\frac{Z\Psi F}{2RT}\right)$$

ε and ε_0 are the dielectric constant of water and the permittivity of free space, respectively. c is the molar electrolyte concentration, and Z the ionic charge.

How to put up an adsorption matrix: A simple example:

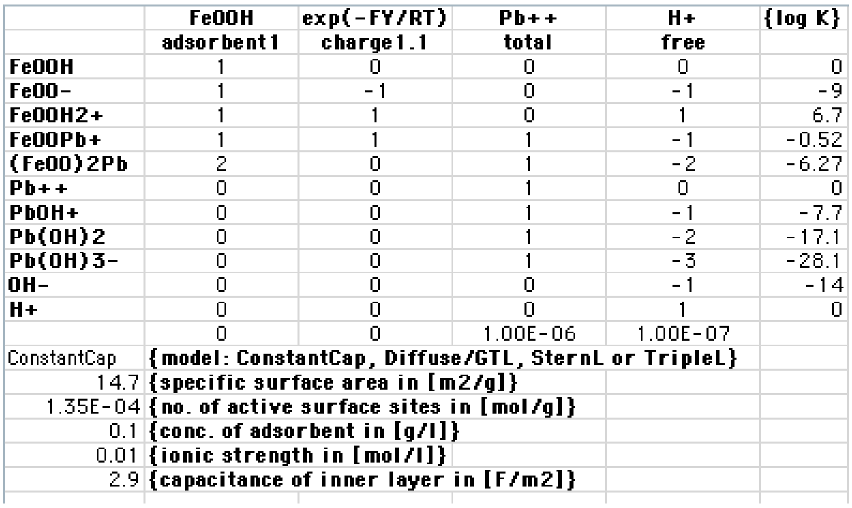
Pb adsorbs to Fe-oxide particles under near neutral and alkaline conditions. We need additional information on the nature and chemical behavior of the suspended particles such as: Specific surface area, concentration of surface sites, ionic strength and capacitance of the electric double layer. Choose the model you wish to use to account for the electrostatic interactions between charges: You have the choice of either the Constant Capacitance Model ('**ConstantCap**'), the Diffuse Double Layer Model or the Generalized Two Layer Model ('**Diffuse/GTL**'), the Basic Stern Layer Model ('**SternL**') or the Triple Layer Model ('**TripleL**'). With *ChemEQL* you have **the possibility of choosing either (up to five) different types of adsorbents or (up to three) different types of surface sites on one type of adsorbent.**

Adsorbing surface sites and surface charges are introduced in the matrix as components. We assume here one type of particle with one type of surface site, and the formation of two types of surface complexes which differ only in stoichiometry, modeled as mono- and bidentate surface complexes of Pb. Adsorption matrices cannot be put up from the library but must be organized in EXCEL. In the adsorption matrix surface site(s) are treated like ordinary ligands:

FeOOH		-> $[FeOOH] = 10^{0}\cdot [FeOOH]$
$FeOOH \Leftrightarrow \mathbf{FeOO^{-}} + H^{+}$	$\frac{[FeOO^{-}][H^{+}]}{[FeOOH]} = 10^{-9}$	-> $[FeOO^{-}] = 10^{-9}\cdot[FeOOH][H^{+}]^{-1}$
$FeOOH\ ^{+}\ H^{+} \Leftrightarrow \mathbf{FeOOH_2^{+}}$	$\frac{[FeOOH_2^{+}]}{[FeOOH][H^{+}]} = 10^{6.7}$	-> $[FeOOH_2^{+}] = 10^{6.7}\cdot[FeOOH][H^{+}]$
$\mathbf{Pb^{2+}}$		-> $[Pb^{+2}] = 10^{0}\cdot [Pb^{+2}]$
$FeOOH + Pb^{+2} \Leftrightarrow \mathbf{FeOOPb^{+}} + H^{+}$	$\frac{[FeOOPb^{+}][H^{+}]}{[FeOOH][Pb^{+2}]} = 10^{-0.52}$	-> $[FeOOPb^{+}] = 10^{-0.52}\cdot[FeOOH][Pb^{+2}][H^{+}]^{-1}$
$2FeOOH + Pb^{+2} \Leftrightarrow \mathbf{(FeOO)_2Pb} + 2H^{+}$	$\frac{[(FeOO)_2Pb][H^{+}]^2}{[FeOOH]^2[Pb^{+2}]} = 10^{-6.27}$	-> $[(FeOO)_2Pb] = 10^{-6.27}\cdot[FeOOH]^2[Pb^{+2}][H^{+}]^{-2}$

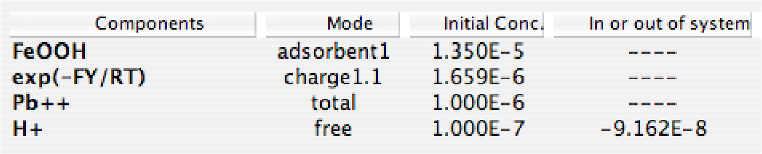
Add the additional information required at the bottom of the matrix as shown in the following example. Make sure to use correct codes for double layer models and correct modes for components: The column containing the particulate ligand must be called '**adsorbent1**' (you can have up to five different particles; see further examples. Call them '**adsorbent2**', '**adsorbent3**' etc.). If you wish to use different types of surface sites (up to three are possible) call these components '**adsorbent1.1**', '**adsorbent1.2**' etc. The numbers indicate 'adsorbent(*whichParticle.whichSite*)'. Columns containing charges must be called '**charge1.1**', '**charge2.1**', etc for Constant Capacitance and Diffuse Double Layer models. The Triple Layer model requires three charge components: '**charge1.1**', '**charge1.2**', '**charge1.3**' for each adsorbing type of particles, the numbers indicating 'charge(*whichParticle.whichCharge*)'. See examples 11-16 later.

0 is entered for the concentration of adsorbent (since the program will calculate concentrations from the input of other parameters and does not require this input), and **0** for the sum of charges (for Constant Capacitance and Diffuse Layer models where there is only one double layer).



	FeOOH adsorbent1	exp(-FY/RT) charge1.1	Pb++ total	H+ free	{log K}
FeOOH	1	0	0	0	0
FeOO-	1	-1	0	-1	-9
FeOOH2+	1	1	0	1	6.7
FeOOPb+	1	1	1	-1	-0.52
(FeOO)2Pb	2	0	1	-2	-6.27
Pb++	0	0	1	0	0
PbOH+	0	0	1	-1	-7.7
Pb(OH)2	0	0	1	-2	-17.1
Pb(OH)3-	0	0	1	-3	-28.1
OH-	0	0	0	-1	-14
H+	0	0	0	1	0
	0	0	1.00E-06	1.00E-07	
ConstantCap	{model: ConstantCap, Diffuse/GTL, SternL or TripleL}				
14.7	{specific surface area in [m2/g]}				
1.35E-04	{no. of active surface sites in [mol/g]}				
0.1	{conc. of adsorbent in [g/l]}				
0.01	{ionic strength in [mol/l]}				
2.9	{capacitance of inner layer in [F/m2]}				

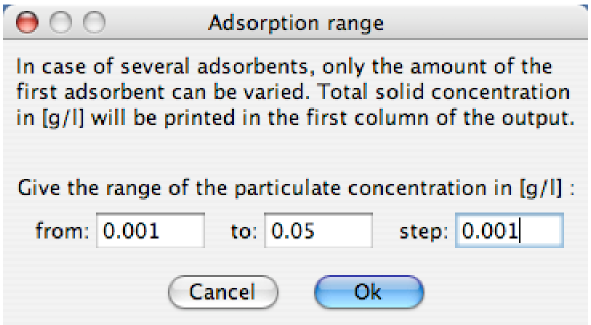
The above matrix is located in the demo folder and is named **'FeAdsorption.cql'**, and calculation can be performed directly. The lower part of the data window contains the total concentration of adsorption sites as calculated from the input of specific surface area, number of active surface sites, and concentration of adsorbent. The total concentration of surface charges sums up all charges of surface species and expresses them in moles per liter.



Components	Mode	Initial Conc.	In or out of system
FeOOH	adsorbent1	1.350E-5	----
exp(-FY/RT)	charge1.1	1.659E-6	----
Pb++	total	1.000E-6	----
H+	free	1.000E-7	-9.162E-8

Titration of a solution with particles

If you use matrices with adsorption to particulate surfaces you have the additional option to titrate your system with particles, ie. to **vary the particle concentration in a specified range**, much similar to the option of varying the concentration of a component. Choose ***Adsorption range...*** from the ***Options*** menu, and enter the range of concentrations of your particulate matter.



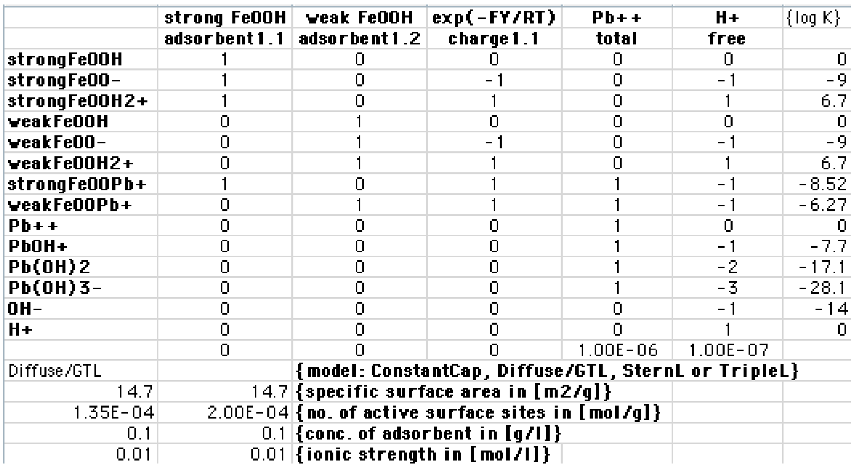
In case of several adsorbents, only the amount of the first adsorbent can be varied. Total solid concentration in [g/l] will be printed in the first column of the output.

Give the range of the particulate concentration in [g/l] :

from: 0.001 to: 0.05 step: 0.001

The Generalized Two Layer Model

Dzombak and Morel in their first compilation of experimental adsorption data recommend for pragmatic reasons the use of the **Generalized Two Layer Model**. The Generalized Two Layer Model basically consists of the **Diffuse Double Layer Model** combined with the **Surface Precipitation Model** by *Farley et al (1985)*, which can account for the eventual formation of a solid solution phase on the surface at high sorbate to sorbent ratios. The diffuse layer model considers one layer of surface charges and a diffuse layer of counter charges in solution. A capacitance is not needed. The authors recommend using one surface site to model anion adsorption data, and two site types ('strong' and 'weak' surface sites, ***both site types are considered to have the same proton binding characteristics!***) to model cation adsorption data. They find this basic two-layer model adequate for the description of all but the highest cation concentrations. An example for the cation surface complexation with two site types on one sort of particles as recommended by *Dzombak and Morel*, however without surface precipitation, is given below. (Example 4.2). It is named 'GTL.mat' in your demo folder.



	strong FeOOH	weak FeOOH	exp(-FY/RT)	Pb++	H+	{log K}
	adsorbent1.1	adsorbent1.2	charge1.1	total	free	
strongFeOOH	1	0	0	0	0	0
strongFeOO-	1	0	-1	0	-1	-9
strongFeOOH2+	1	0	1	0	1	6.7
weakFeOOH	0	1	0	0	0	0
weakFeOO-	0	1	-1	0	-1	-9
weakFeOOH2+	0	1	1	0	1	6.7
strongFeOOPb+	1	0	1	1	-1	-8.52
weakFeOOPb+	0	1	1	1	-1	-6.27
Pb++	0	0	0	1	0	0
PbOH+	0	0	0	1	-1	-7.7
Pb(OH)2	0	0	0	1	-2	-17.1
Pb(OH)3-	0	0	0	1	-3	-28.1
OH-	0	0	0	0	-1	-14
H+	0	0	0	0	1	0
	0	0	0	1.00E-06	1.00E-07	
Diffuse/GTL		{model: ConstantCap, Diffuse/GTL, SternL or TripleL}				
14.7	14.7	{specific surface area in [m2/g]}				
1.35E-04	2.00E-04	{no. of active surface sites in [mol/g]}				
0.1	0.1	{conc. of adsorbent in [g/l]}				
0.01	0.01	{ionic strength in [mol/l]}				

Note that no capacitance is needed in the input matrix. At high sorbate/sorbent ratios precipitation of the hydroxide or carbonate of the adsorbing cation on the surface was observed by *Farley et al. (1985)*. Their model considers the formation of a new surface phase. To describe the formation of a 'solid solution' on the surface solubility products determined for bulk solutions are applied. All surface reactions need to be described as surface precipitation reactions. A new component is introduced in order to describe the fractions of sorbate and sorbent in the solid solution. An example for the sorption and precipitation reactions of a cation M^{2+} on a hydrous oxide $X(OH)_3(s)$ is taken from *Dzombak and Morel (1990), p. 29-32*:

Adsorption of M^{2+} on $X(OH)_3(s)$:

$$\equiv XOH^0 + M^{2+} + 2H_2O \leftrightarrow X(OH)_3(s) + \equiv MOH_2^+ + H^+ \qquad K_M^{app}$$

Precipitation of M^{2+}:

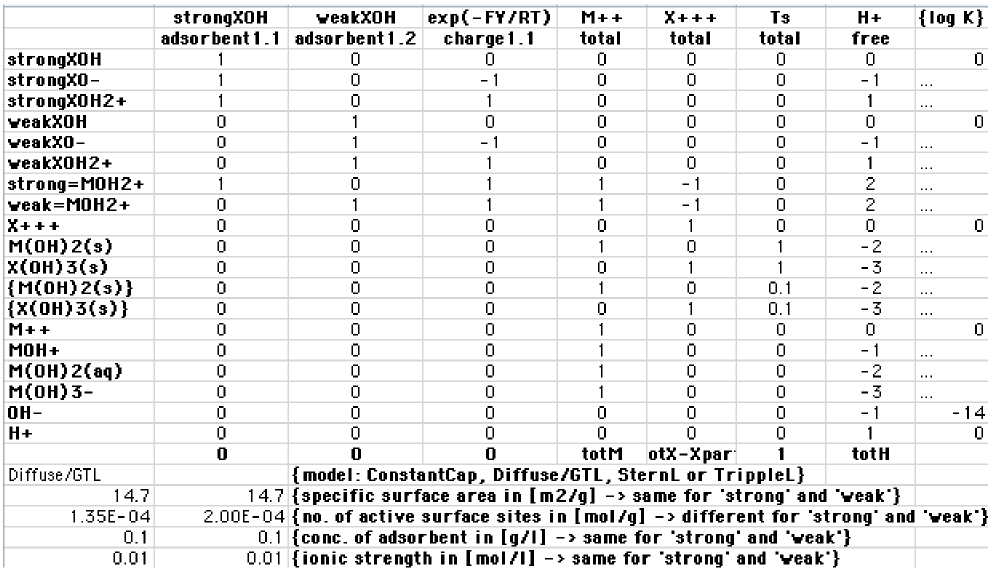
$$\equiv MOH_2^+ + M^{2+} + 2H_2O \leftrightarrow M(OH)_2(s) + \equiv MOH_2^+ + 2H^+ \qquad K_{spM}^{-1}$$

Precipitation of X^{3+}:

$$\equiv XOH^0 + X^{3+} + 3H_2O \leftrightarrow X(OH)_3(s) + \equiv XOH^0 + 3H^+ \qquad K_{spX}^{-1}$$

The adsorption reaction of X^{3+} on $M(OH)_{2(s)}$ can be derived from the above equations and is not shown. The component Ts represents the total mass of solid material in solid solution and is used to express the activity constraint on the solid solution.

The matrix that results from this input and suits the need of the complete 'Generalized Two Layer Model' for cation adsorption including surface precipitation looks like represented in the following table ('GTL-Precip.table' in the demo folder) and only needs to be completed with the appropriate formation constants and concentrations:



	strongXOH	weakXOH	exp(-FY/RT)	M++	X+++	Ts	H+	{log K}
	adsorbent1.1	adsorbent1.2	charge1.1	total	total	total	free	
strongXOH	1	0	0	0	0	0	0	0
strongXO-	1	0	-1	0	0	0	-1	...
strongXOH2+	1	0	1	0	0	0	1	...
weakXOH	0	1	0	0	0	0	0	0
weakXO-	0	1	-1	0	0	0	-1	...
weakXOH2+	0	1	1	0	0	0	1	...
strong=MOH2+	1	0	1	1	-1	0	2	...
weak=MOH2+	0	1	1	1	-1	0	2	...
X+++	0	0	0	0	1	0	0	0
M(OH)2(s)	0	0	0	1	0	1	-2	...
X(OH)3(s)	0	0	0	0	1	1	-3	...
{M(OH)2(s)}	0	0	0	1	0	0.1	-2	...
{X(OH)3(s)}	0	0	0	0	1	0.1	-3	...
M++	0	0	0	1	0	0	0	0
MOH+	0	0	0	1	0	0	-1	...
M(OH)2(aq)	0	0	0	1	0	0	-2	...
M(OH)3-	0	0	0	1	0	0	-3	...
OH-	0	0	0	0	0	0	-1	-14
H+	0	0	0	0	0	0	1	0
	0	**0**	**0**	**totM**	**otX-Xpar**	**1**	**totH**	
Diffuse/GTL		**{model: ConstantCap, Diffuse/GTL, SternL or TrippleL}**						
14.7	14.7	**{specific surface area in [m2/g] -> same for 'strong' and 'weak'}**						
1.35E-04	2.00E-04	**{no. of active surface sites in [mol/g] -> different for 'strong' and 'weak'}**						
0.1	0.1	**{conc. of adsorbent in [g/l] -> same for 'strong' and 'weak'}**						
0.01	0.01	**{ionic strength in [mol/l] -> same for 'strong' and 'weak'}**						

Surfaces characterized by Fractional Surface Charge: The one-pK-model

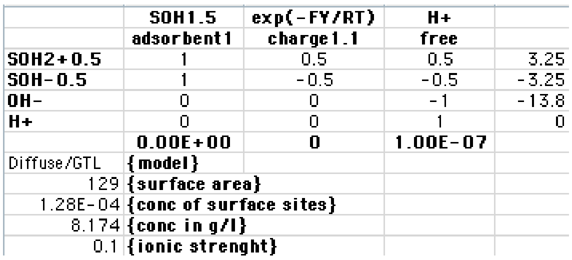
The one-pK-model (*Westall, 1987*) simplifies the description of the acid-base equilibria by assuming only one proton exchange reaction. (The following example and more are published and discussed in the 2nd ed. of *Stumm, 1992*):

$$SOH_2^{+1/2} \leftrightarrow SOH^{-1/2} + H^+ \qquad K_a$$

In fact, a new uncharged component, **$SOH^0_{1.5}$**, was introduced to allow the equilibria to be described with only one protolysis constant:

$$SOH_2^{+1/2} \xleftrightarrow[K_a^{1/2}]{-\frac{1}{2}H^+} SOH_{1.5}^0 \xleftrightarrow[K_a^{1/2}]{-\frac{1}{2}H^+} SOH^{-1/2}$$

The matrix therefore needs the uncharged surface species as a component, and the two species with broken charges:



	SOH1.5	exp(-FY/RT)	H+	
	adsorbent1	charge1.1	free	
SOH2+0.5	1	0.5	0.5	3.25
SOH-0.5	1	-0.5	-0.5	-3.25
OH-	0	0	-1	-13.8
H+	0	0	1	0
	0.00E+00	0	1.00E-07	
Diffuse/GTL	{model}			
129	{surface area}			
1.28E-04	{conc of surface sites}			
8.174	{conc in g/l}			
0.1	{ionic strenght}			

The program calculates the total concentration of surface sites from the entries of the concentration of adsorbent [kg l^{-1}] and the characteristic conc. of surface sites [mol kg^{-1}]. In the column of the surface charges of the species are the differences in surface charge for the reaction considered. The potential difference across the double layer is calculated according to the model chosen, preferably the Diffuse Double Layer model.

Anion or cation sorption is introduced with the following type of equations:

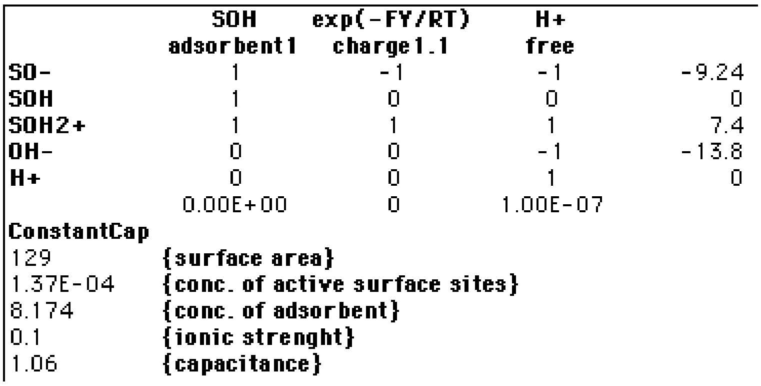
cation: $$SOH^{-1/2} + Me^{2+} \leftrightarrow SOMe^{+1/2} + H^+$$

anion: $$SOH^{-1/2} + HA \leftrightarrow SA^{-1/2} + H_2O$$

Examples

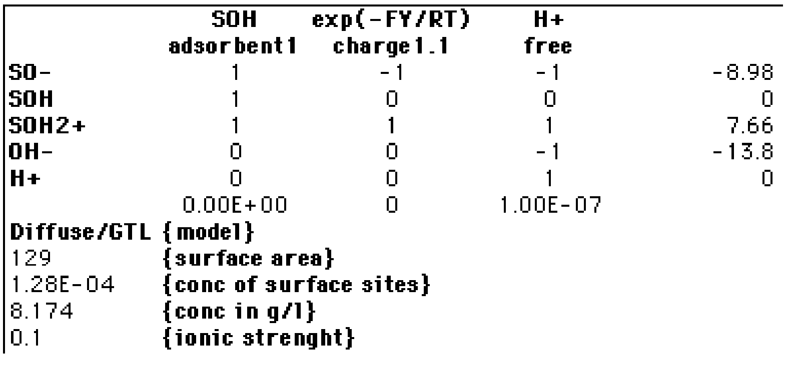
The next three examples show basic input matrices for the four different models. Further examples in the 'examples' chapter will demonstrate the use of several types of adsorbents.

Example for a basic matrix of surface speciation according to the **Constant Capacitance Model** ('ConstantCap.mat' in demo folder):



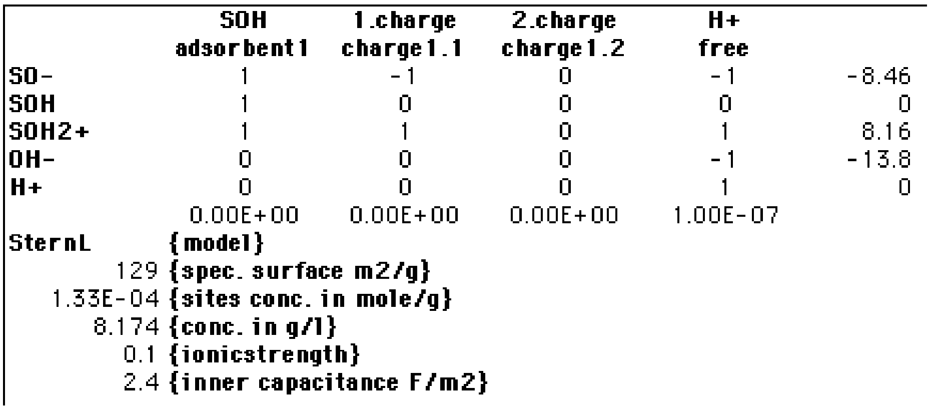
	SOH adsorbent1	exp(-FY/RT) charge1.1	H+ free	
SO-	1	-1	-1	-9.24
SOH	1	0	0	0
SOH2+	1	1	1	7.4
OH-	0	0	-1	-13.8
H+	0	0	1	0
	0.00E+00	0	1.00E-07	
ConstantCap				
129	**{surface area}**			
1.37E-04	**{conc. of active surface sites}**			
8.174	**{conc. of adsorbent}**			
0.1	**{ionic strenght}**			
1.06	**{capacitance}**			

Example for a basic matrix of surface speciation according to the **Diffuse Layer Model,** which is recommended to use by *Dzombak and Morel* ('Diffuse/GTL.mat'):



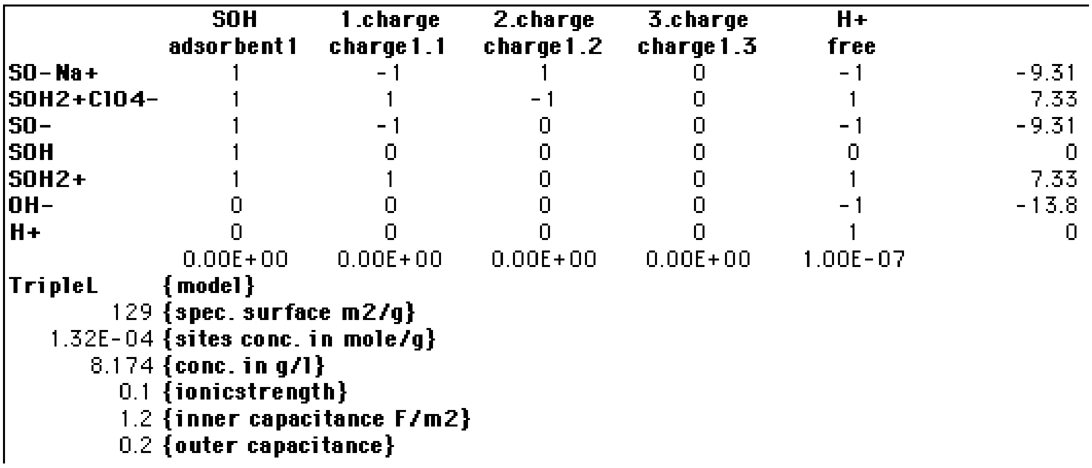
	SOH adsorbent1	exp(-FY/RT) charge1.1	H+ free	
SO-	1	-1	-1	-8.98
SOH	1	0	0	0
SOH2+	1	1	1	7.66
OH-	0	0	-1	-13.8
H+	0	0	1	0
	0.00E+00	0	1.00E-07	
Diffuse/GTL	**{model}**			
129	**{surface area}**			
1.28E-04	**{conc of surface sites}**			
8.174	**{conc in g/l}**			
0.1	**{ionic strenght}**			

Surface speciation according to the **Basic Stern Layer Model**:



```
                  SOH        1.charge    2.charge      H+
               adsorbent1   charge1.1   charge1.2     free
SO-                 1          -1          0           -1         -8.46
SOH                 1           0          0            0            0
SOH2+               1           1          0            1         8.16
OH-                 0           0          0           -1         -13.8
H+                  0           0          0            1            0
               0.00E+00    0.00E+00    0.00E+00    1.00E-07
SternL      {model}
         129 {spec. surface m2/g}
    1.33E-04 {sites conc. in mole/g}
       8.174 {conc. in g/l}
         0.1 {ionicstrength}
         2.4 {inner capacitance F/m2}
```

Surface speciation according to the **Triple Layer Model**:



```
                 SOH        1.charge    2.charge    3.charge      H+
              adsorbent1   charge1.1   charge1.2   charge1.3     free
SO-Na+             1          -1           1           0          -1          -9.31
SOH2+ClO4-         1           1          -1           0           1           7.33
SO-                1          -1           0           0          -1          -9.31
SOH                1           0           0           0           0              0
SOH2+              1           1           0           0           1           7.33
OH-                0           0           0           0          -1          -13.8
H+                 0           0           0           0           1              0
              0.00E+00    0.00E+00    0.00E+00    0.00E+00    1.00E-07
TripleL     {model}
         129 {spec. surface m2/g}
    1.32E-04 {sites conc. in mole/g}
       8.174 {conc. in g/l}
         0.1 {ionicstrength}
         1.2 {inner capacitance F/m2}
         0.2 {outer capacitance}
```

Literature:

Dzombak D.A., and F.M.M. Morel: **Surface Complexation Modelling.** Wiley Interscience (1990).

Farley K.J., D.A. Dzombak, F.M.M. Morel: **A surface prepcipitation model for the sorption of cations on metal oxides.** J. Colloid Interface Sci. 106, 226-242 (1985).

Stumm W., and J.J. Morgan: **Aquatic Chemistry**, 3rd ed. (1996).

Stumm W.: **Chemistry of the solid-water interface.** Wiley Interscience, 1992.

Westall J., and H. Hohl**: A comparison of electrostatic models for the oxide-solution interface.** Adv. Coll. Interface Sci., 12, 265-294 (1980).

Westall J.: **Adsorption mechanisms in aquatic surface chemistry.** *in:* Aquatic surface chemistry, ed. by W. Stumm, John Wiley and Sons, New York, 3-32 (1987).

Redox Reactions

The (microbially mediated) redox equilibrium between N(V) and N(-III) is calculated as an example. The electron, which is part of these reactions, must be a component. The following equations are in the library and can be accessed easily:

$\mathbf{NO_3^-}$ -> $[NO_3^-] = 10^{0} \cdot [NO_3^-]$

$NO_3^- + 9H^+ + 8e^- \Leftrightarrow \mathbf{NH_3} + 3H_2O$ $\frac{[NH_3]}{[NO_3^-][H^+]^9[e^-]^8} = 10^{109.9}$ -> $[NH_3] = 10^{109.9} \cdot [NO_3^-][e^-]^8[H^+]^9$

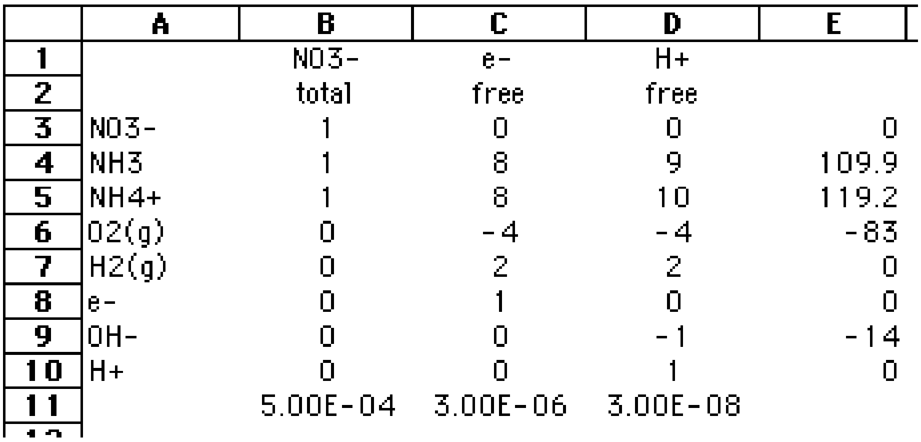
$NO_3^- + 10H^+ + 8e^- \Leftrightarrow \mathbf{NH_4^+} + 3H_2O$ $\frac{[NH_4^+]}{[NO_3^-][H^+]^{10}[e^-]^8} = 10^{119.2}$ -> $[NH_4^+] = 10^{119.2} \cdot [NO_3^-][e^-]^8[H^+]^{10}$

$2H_2O \Leftrightarrow \mathbf{O_{2(g)}} + 4H^+ + 4e^-$ $[O_{2(g)}][e^-]^4[H^+]^4) = 10^{-83}$ -> $[O_{2(g)}] = 10^{-83}[e^-]^{-4}[H^+]^{-4}$

$2H^+ + 2e^- \Leftrightarrow \mathbf{H_{2(g)}}$ $\frac{[H_{2(g)}]}{[e^-]^2[H^+]^2} = 10^{0}$ -> $[H_{2(g)}] = 10^{0} \cdot [e^-]^2[H^+]^2$

$\mathbf{e^-}$ -> $[e^-] = 10^{0} \cdot [e^-]$

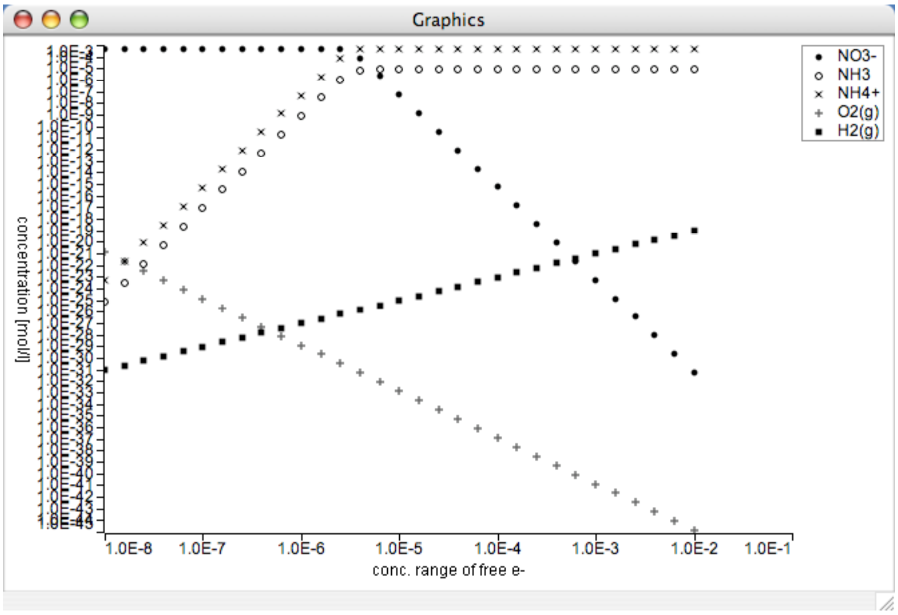
$\mathbf{H^+}$ -> $[H^+] = 10^{0} \cdot [H^+]$



	A	B	C	D	E
1		NO3-	e-	H+	
2		total	free	free	
3	NO3-	1	0	0	0
4	NH3	1	8	9	109.9
5	NH4+	1	8	10	119.2
6	O2(g)	0	-4	-4	-83
7	H2(g)	0	2	2	0
8	e-	0	1	0	0
9	OH-	0	0	-1	-14
10	H+	0	0	1	0
11		5.00E-04	3.00E-06	3.00E-08	

This matrix is stored in the demo folder under the name 'Redox.mat'

To represent the development of the N(V)-N(-III) couple in a pε-range choose ***Component range...*** from the ***Options*** menu. Select the e- component and enter a logarithmic interval from -8 to -2 in steps of 0.25. (The output format is now set to ***logarithmic*** as you can check in the ***Format*** item). Select ***Graphics...*** and mark the first five items to obtain the curves. ***Go*** will calculate the following graph:



NO_3^- prevails in the region where log e^- is smaller than -5.5, and NH_4^+ under more reducing conditions where log e^- >-5.5.

Kinetics

ChemEQL allows the calculation of species distribution in a system that is controlled by one rate limiting chemical reaction. The chemical speciation is assumed to be much faster than the selected kinetic reaction. The program covers the most common types of kinetic rate equations. (No consecutive kinetic reactions are possible, however.)

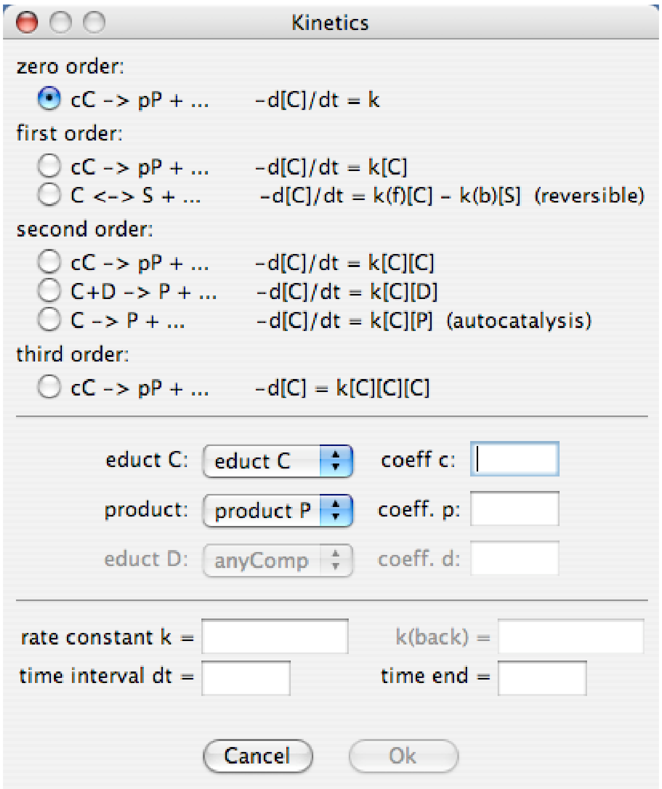
In a first step the program performs a speciation calculation that results in the concentrations of the species before any kinetic reaction takes effect ($t_{kin} = 0$). The equilibrium concentration of the educt species (E) is then set to the start concentration of the educt for the kinetic calculation. The following kinetic calculation therefore uses the concentration of the educt species (and not the total concentration of the educt component). The amount of E used up in this process is subtracted from the total concentration of E, and the product (P) produced by this step is added to the total concentration of P. A speciation calculation is then performed and the result given in the output. If the kinetic reaction is reversible (includes a backreaction) or autocatalytic (product enhances speed of reaction), the concentration of P that takes part in the kinetic calculation is of course also the free concentration of the product species and not the total concentration of P.

The input matrix must be organized such that ***educt and product are components:***

	Educt	**Product**	**...**	**H+**	{log K}
	total	***total***	**...**	**...**	
Educt	1	0	0	0	0
Product	0	1	0	0	0
ProdSpecies1	...	...	...	...	...
ProdSpecies2	...	...	...	...	...
...	...	...	...	...	...
OH-	0	0	0	-1	-14
H+	0	0	0	1	0
	startConc	**usually=0**	**...**	**...**	

Be aware of the dimensions of the kinetic constants! Use **moles l^{-1} sec^{-1} (zero order), sec^{-1} (1st order), l moles^{-1} sec^{-1} (2nd order) etc.** or remember that the time scale of your input will change the output accordingly.

The following dialog appears if you choose ***Kinetics...*** from the menu:



Kinetics

zero order:
● cC -> pP + ...   -d[C]/dt = k
first order:
○ cC -> pP + ...   -d[C]/dt = k[C]
○ C <-> S + ...   -d[C]/dt = k(f)[C] - k(b)[S] (reversible)
second order:
○ cC -> pP + ...   -d[C]/dt = k[C][C]
○ C+D -> P + ...   -d[C]/dt = k[C][D]
○ C -> P + ...   -d[C]/dt = k[C][P] (autocatalysis)
third order:
○ cC -> pP + ...   -d[C] = k[C][C][C]

educt C: educt C   coeff c:
product: product P   coeff. p:
educt D: anyComp   coeff. d:

rate constant k =   k(back) =
time interval dt =   time end =

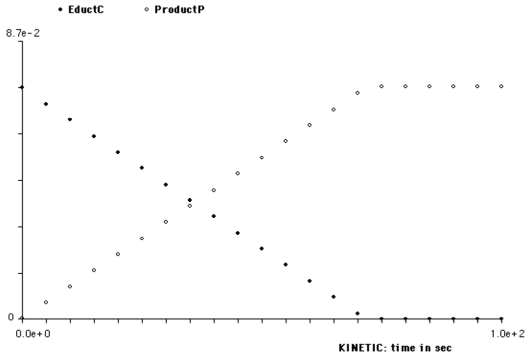
Choose the desired rate law, define educt and product of your system, enter the stoichiometric coefficients, rate constants, and time interval. For graphical display of one or more species choose ***Graphics...*** from the ***Options*** menu after closing the kinetic dialog.

A few basic examples for simple Kinetic calculations without speciation are given below. The following general matrix can be used to demonstrate the function of all types of kinetics:

	Educt C *total*	Product P *total*	anyComp. *total*	H+ *free*	
Educt C	1	0	0	0	0
Product P	0	1	0	0	0
any Species	0	0	1	0	0
more Species	0	0	1	-2	-12
OH-	0	0	0	-1	-14
H+	0	0	0	1	0
	7.2E-2	3.0E-4	1.0E-6	1.0E-5	

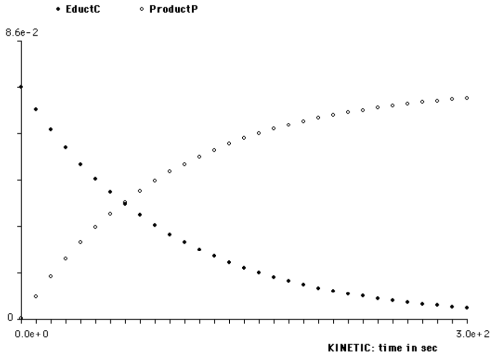
Zero order:

(k=10^{-3}, t=5-100)



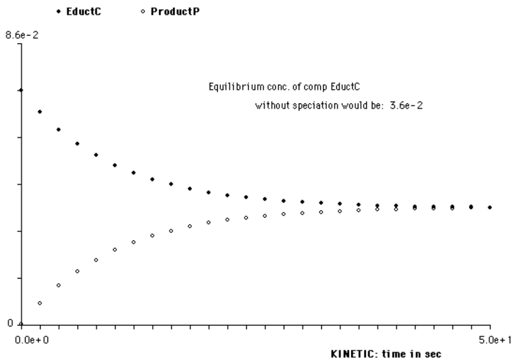
First order:

(k=0.01, t=10-300)



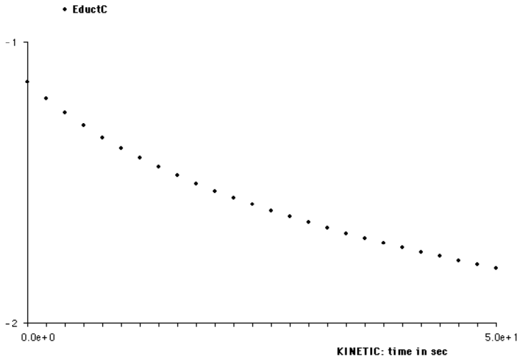
Reversible:

(k=0.05, k_{back}=0.05, t=2-50)



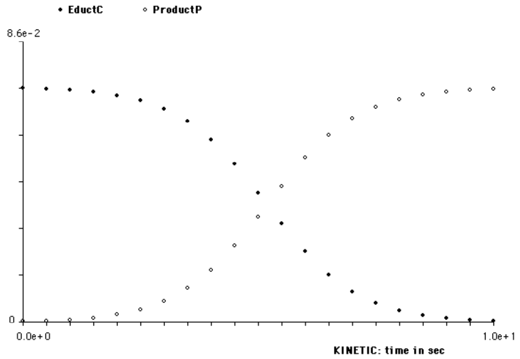
Second order in C:

(k=1, t=2-50, logarithmic scale)



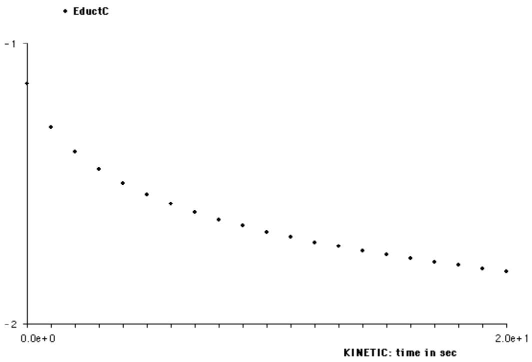
Second order overall, but first order in C and D: (k=1, t=2-50, logarithmic scale)

Autocatalysis: (k=14.6, t=0.5-10, Example see *Frost&Pearson, Kinetics and Mechanism, Wiley 1961, p19*)



Third order:

(k=100, t=1-20, logarithmic scale)



Integrated rate laws

zero order: **cC → P**

$$\left[C\right]_t = C_0 - ckt$$

first order: **cC → P**

$$\left[C\right]_t = C_0 \cdot \exp^{-ckt}$$

C ↔ P (reversible)

$$\left[C\right]_t = C_0 \frac{k + k' \cdot \exp^{(k+k')t}}{\left(k + k'\right) \cdot \exp^{(k+k')t}}$$

Second order: **cC → P**

$$\left[C\right]_t = \frac{C_0}{C_0 ckt + 1}$$

cC + dD → P

$$\left[C\right]_t = C_0 - \frac{cC_0 D_0 \left(\exp^{kt(C_0 - D_0)} - 1\right)}{dC_0 \exp^{kt(C_0 - D_0)} - cD_0}$$

$$\left[D\right]_t = D_0 - \frac{d}{c}\left(C_0 - C_t\right)$$

cC → pP (autocatalysis)

$$\left[C\right]_t = \frac{1}{c}\left\{C_0 - \frac{C_0 P_0 \left(p \cdot \exp^{kt(C_0 + P_0)} - c\right)}{cC_0 + pP_0 \cdot \exp^{kt(C_0 + P_0)}}\right\}$$

$$\left[P\right]_t = \frac{1}{c}\left\{C_0 + P_0 - c\left[C\right]_t\right\}$$

Third order: **cC → P**

$$\left[C\right]_t = \frac{C_0}{\sqrt{2cktC_0^2 + 1}}$$

nth order: **cC → P**

$$\left[C\right]_t = \frac{C_0}{\left(\left(n - 1\right)cktC_0^{n-1} + 1\right)^{1/n}}$$

pX-pY diagrams

The pX-pY diagrams option is of use in the calculation of the prevailing dissolved species or solid phases of a component under varying conditions of another parameter like the redox potential (pε), a complex forming ligand, or a ligand that forms solid phases with the component. Calculation is possible only for species derived from one single component (eg. all dissolved complexes and solid phases for Fe(II) and Fe(III) if either Fe^{2+} or Fe^{3+} is chosen as a component). **All relevant species that are to appear in the diagram must have priority in the list of species. Species that are solid phases must carry the code '(s)' in their names, gaseous species the code '(g)', so the program can recognize them.**

The option shall be demonstrated with two examples: 1) The calculation of the pε-pH-diagram for water, and 2) the pε-pH-diagram for the Fe-CO_2-system as exemplified in *Stumm and Morgan, Aquatic Chemistry (1981), p. 446*.

Example 1: pε-pH-diagram for water

What are the redox boundaries for the existence of water? At what pH and redox potential is H_2O either reduced or oxidized?

The species occurring in the system are: H_2O, $H_2(g)$, $O_2(g)$, e^-, OH^-, and H^+

Three reactions have to be taken into consideration:

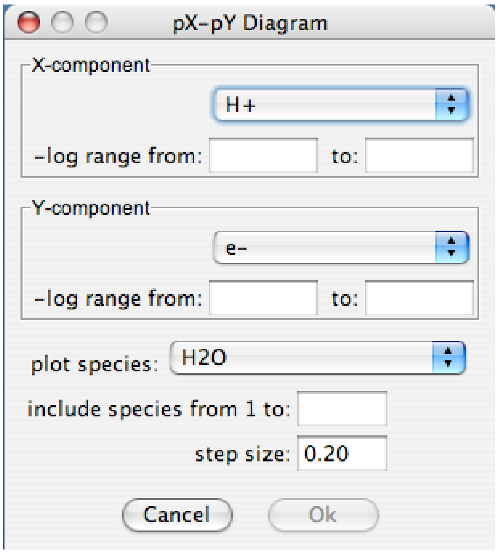
a. the oxidation:	$2H_2O \Leftrightarrow O_2 + 4e^- + 4H^+$	log K = -83
b. the reduction:	$2H^+ + 2e^- \Leftrightarrow H_2$	log K = 0
c. autocatalysis of water:	$H_2O \Leftrightarrow H^+ + OH^-$	log K = -14

The program calculates speciation in the desired steps, searches for the species with the highest concentration, and compares with the species with the highest concentration found in the last interval. Gaseous species (whose name must contain the code '**(g)**') are recognized as dominating when their partial pressure is at least 1atm, and solid phases '**(s)**' when their solubility product is exceeded. Bordering concentrations are calculated by an iterative procedure converging when the error is smaller than .001.

The abovementioned six species are described with three components (H_2O, e^-, and H^+), and constitute the input matrix. Input concentrations are 55.55 mol/l for water, and any concentration for e^- and H^+, since these concentrations will be altered by the program according to user inputs by the pX-pY-dialog. The modes for these two components must be 'free'. (The matrix is 'pXpY-H2O.mat' in the demo folder):

	H2O	**e-**	**H+**	
	total	***free***	***free***	
O2(g)	2	-4	-4	-83
H2(g)	0	2	2	0
H2O	1	0	0	0
e-	0	1	0	0
OH-	0	0	-1	-14
H+	0	0	1	0
	55.55	**1e+3**	**1e-3**	

Choosing ***pXpY diagram...*** from the menu will lead you to the following dialog window:



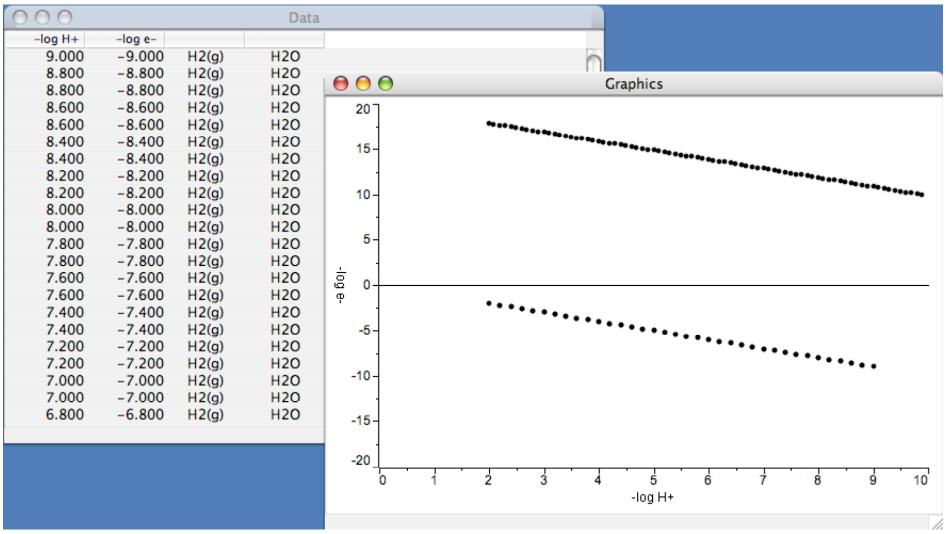
X-component: H+
-log range from: to:

Y-component: e-
-log range from: to:

plot species: H2O
include species from 1 to:
step size: 0.20

Choose the X and Y component and give the range in negative logarithms (pX = -log X). Choose pH range 3 to 9 and pε range -10 to +20. The **main component** that is **common to all species of interest** is H_2O. Species from 1-3 are to be included in the graphic (i.e. O_2 (g), H_2 (g), H_2O). The suggested step size of 0.2 refers to the logarithmic units of both, pX and pY, i.e. pH and pε.

Filling in the questionnaire, closing, and pressing ***Go* will automatically activate *Graphics***, and you will obtain the following diagram:



-log H+	-log e-		
9.000	-9.000	H2(g)	H2O
8.800	-8.800	H2(g)	H2O
8.800	-8.800	H2(g)	H2O
8.600	-8.600	H2(g)	H2O
8.600	-8.600	H2(g)	H2O
8.400	-8.400	H2(g)	H2O
8.400	-8.400	H2(g)	H2O
8.200	-8.200	H2(g)	H2O
8.200	-8.200	H2(g)	H2O
8.000	-8.000	H2(g)	H2O
8.000	-8.000	H2(g)	H2O
7.800	-7.800	H2(g)	H2O
7.800	-7.800	H2(g)	H2O
7.600	-7.600	H2(g)	H2O
7.600	-7.600	H2(g)	H2O
7.400	-7.400	H2(g)	H2O
7.400	-7.400	H2(g)	H2O
7.200	-7.200	H2(g)	H2O
7.200	-7.200	H2(g)	H2O
7.000	-7.000	H2(g)	H2O
7.000	-7.000	H2(g)	H2O
6.800	-6.800	H2(g)	H2O

Save the calculated points that appeared in the data window by choosing ***Save data...*** from the ***File*** menu to use a professional drawing software.

Example 2: pε-pH-diagram for the Fe - CO_2 - H_2O system

(from *Stumm and Morgan, Aquatic Chemistry, 1981, fig. 7.7.*)

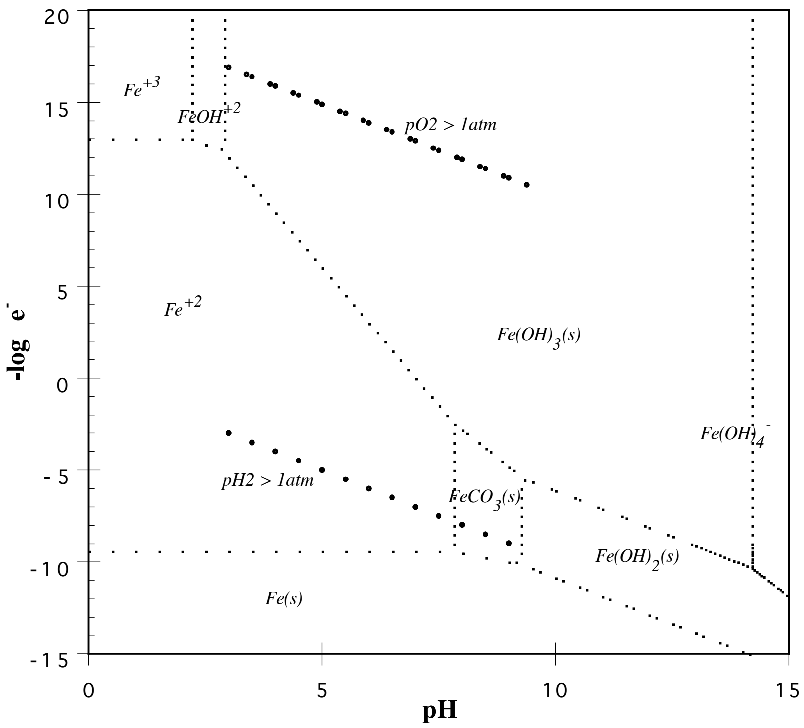
The various dissolved complexes and solid phases of iron, reduced and oxidized, that prevail under certain conditions of pH and redox potential are calculated here according to thermodynamic equilibrium constants. It is quite a task to collect all equilibrium constants, and comparing them with the constants used in *Stumm and Morgan* or *Sigg und Stumm (Aquatische Chemie, 1994)*, one will find that these are not consistent throughout the graphs. Small changes in the solubility products for $Fe(OH)_2$(s) and $FeCO_3$(s) lead to marked differences in the region of existence for $FeCO_3$ (s).

Reactions relevant to the system and its constants are collected in the following matrix ('pXpY-Fe.mat' in the demo folder). Note that the formation of all iron species is formulated with Fe^{2+}:

	Fe++	**HCO3-**	**e-**	**H+**	
	total	***total***	***free***	***free***	
Fe++	1	0	0	0	0
FeOH+	1	0	0	-1	-9.5
Fe(OH)2(aq)	1	0	0	-2	-20.6
Fe(OH)3-	1	0	0	-3	-31
Fe(OH)2(s)	1	0	0	-2	-12.1
FeCO3(aq)	1	1	0	-1	-5.6
FeHCO3-	1	1	0	0	2.4
FeCO3(s)	1	1	0	-1	0.2
Fe(s)	1	0	2	0	-13.8
Fe+++	1	0	-1	0	-13.0
FeOH++	1	0	-1	-1	-15.2
Fe(OH)2+	1	0	-1	-2	-20.2
Fe(OH)4-	1	0	-1	-4	-35.2
Fe(OH)3(s)	1	0	-1	-3	-16.0
H2CO3	0	1	0	1	6.3
HCO3-	0	1	0	0	0
CO3--	0	1	0	-1	-10.3
e-	0	0	1	0	0
OH-	0	0	0	-1	-14
H+	0	0	0	1	0

1.0E-51.0E-31.0E+71.0E-7

The diagram is calculated for a total iron concentration of 10^{-5} mol/l and a total bicarbonate concentration of 10^{-3} mol/l. Combined with the data from example 1, the diagram looks as follows and can easily be completed with a few lines:



The square in the lower right corner was calculated with higher resolution to clearly recognize the slope of the border between $Fe(OH)_2$(s) and $Fe(OH)_4^-$.

Examples

1. All components dissolved, total concentrations given

Complexes of Pb(II) with EDTA and NTA	ex01.mat
Titration curve for Na_3PO_4 with acid	ex02.mat
Titration curve for H_3PO_4 with base	ex03.mat

2. All components dissolved, free concentrations of some components are given

constant pH: Complexes of Mercury (II)	ex04.mat
constant p_{CO_2}: Equilibrium with a soda solution	ex05.mat
constant free conc. of a species: Metal buffer for $Cu^{2+}(aq)$	ex06.mat

3. Dissolution of one (or more) solid phase

Dissolution diagram of $Cu(OH)_2(s)$	ex07.mat
The $CaCO_3$ / CO_2 - system	ex08.mat
Dissolution of $Ca_4Al_2O_6SO_4 \cdot 12H_2O$	ex09.mat
Dissolution of several solid phases	ex10.mat

4. Precipitation of one (or more) solid phases

Precipitation of $PbCO_3(s)$	ex11.mat

5. Adsorption to particulate surfaces

-one particulate surface or one type of surface site respectively

Surface speciation of γ-Al_2O_3 in 0.1M $NaClO_4$ at pH 7

Constant Capacitance Model	ex12.mat
Diffuse Layer Model / Generalized Two Layer Model	ex13.mat
Basic Stern Layer Model	ex14.mat
Triple Layer Model	ex15.mat
Adsorption of lead on goethite	ex16.mat

-two or more particulate surface types

Constant Capacitance Model	ex17.mat
Diffuse Layer / Generalized Two Layer Model	ex18.mat
Basic Stern Layer Model	ex19.mat
Triple Layer Model	ex20.mat

-Several types of surface sites on one type of particle

Diffuse Layer / Generalized Two Layer Model	ex21.mat

6. pXpY Diagrams

The S(VI), S(0), S(-II) - System	ex22.mat
The Chlorine System	ex23.mat

7. Solubility Diagrams

The Iron - CO_2 System	ex24.mat
The $PbCO_3$ - $PbSO_4$ System	ex25.mat

1. All components dissolved, total concentrations given

Complexes of Pb(II) with EDTA and NTA(ex01.mat)

Equilibrium concentrations of all species in a solution made from 10^{-6} M Pb(II), $2 \cdot 10^{-6}$ M H_4EDTA and 10^{-5} M Na_3NTA:

	Pb++	**H4EDTA**	**NTA---**	**H+**	
	total	***total***	***total***	***total***	
Pb++	1	0	0	0	0
PbOH+	1	0	0	-1	-7.7
Pb(OH)2	1	0	0	-2	-17.1
Pb(OH)3-	1	0	0	-3	-28.1
PbNTA-	1	0	1	0	12.6
PbEDTA--	1	1	0	-4	-3.96
PbHEDTA-	1	1	0	-3	-0.76
EDTA----	0	1	0	-4	-23.76
HEDTA---	0	1	0	-3	-12.64
H2EDTA--	0	1	0	-2	-3.66
H3EDTA-	0	1	0	-1	-2.72
H4EDTA	0	1	0	0	0
NTA---	0	0	1	0	0
HNTA--	0	0	1	1	9.71
H2NTA-	0	0	1	2	12.19
H3NTA	0	0	1	3	13.99
H4NTA+	0	0	1	4	14.79
OH-	0	0	0	-1	-14
H+	0	0	0	1	0
	1e-6	**2e-6**	**1e-5**	**0**	

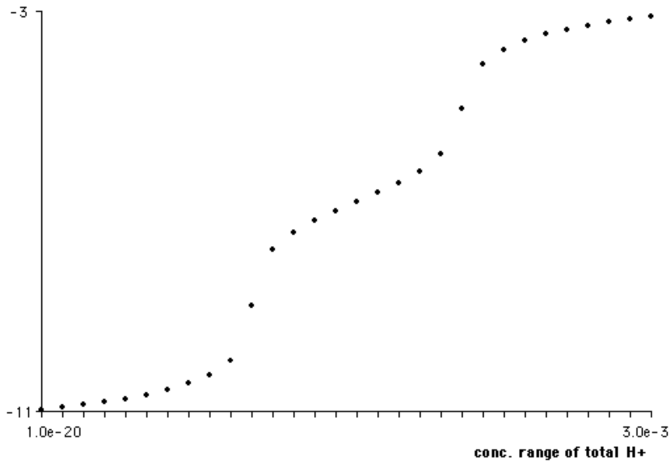
Choose ***Go*** from the ***Run*** menu...

Titration of Na_3PO_4 with strong acid (ex02.mat)

Say we want to calculate the **Titration of a 10^{-3} M solution of Na_3PO_4 with strong acid:** The matrix can be collected from the library. Na+ is omitted since it does not take part in any reaction.

	PO4--- ***total***	**H+** ***total***	
PO4---	1	0	0
HPO4--	1	1	12
H2PO4-	1	2	18.8
H3PO4	1	3	20.9
OH-	0	-1	-14
H+	0	1	0
	1e-3	**0**	

Choose ***Component range*** from the ***Option*** menu. Select H+ (since we titrate with strong acid) and give a range for the amount of strong acid added per liter, eg. from 0 to 3e-3 in steps of 1e-4. (A remark will follow your attempt to enter a concentration of 0, and it will be changed to a very small number). If you wish a graphical representation of the titration curve, change the output format from ***linear*** to ***logarithmic*** (since we want to see the pH in dependence of acid added), select the 'H+' species in the ***Graphic*** item of the ***Options*** menu, and press ***Go***:

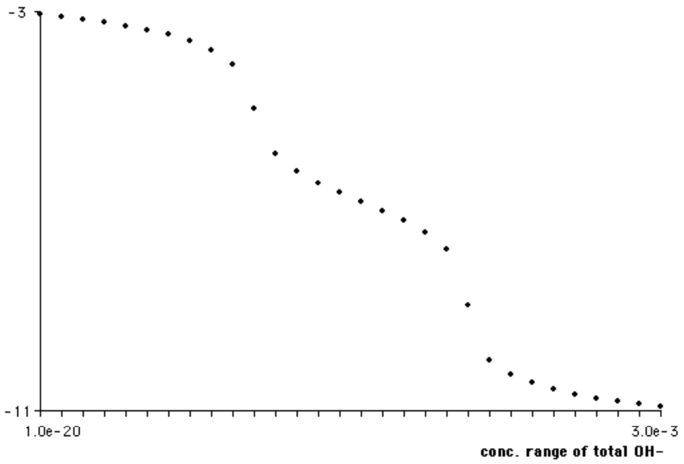


Titration of H_3PO_4 with strong base (ex03.mat)

Calculate a titration curve to the titration of a 10^{-3} M solution of H_3PO_3 with strong base! For this task select a matrix with 'H3PO4' and 'H+', then choose ***Replace H+ by OH-*** from the Matrix menu. You should obtain:

	H3PO4 ***total***	**OH-** ***total***	
PO4---	1	3	21.1
HPO4--	1	2	19.1
H2PO4-	1	1	11.9
H3PO4	1	0	0
H+	0	-1	-14
OH-	0	1	0
	1e-3	**0**	

Choose ***Component range*** under the ***Option*** menu and give a range for the amount of OH^- added per liter (eg. from 0 to $3 \cdot 10^{-3}$ in steps of 10^{-4}). For graphical representation of the titration curve (pH vs. base added) choose the 'H+' species in ***Graphics...*** and change the format from ***linear*** to ***logarithmic***. The following titration curve should be obtained:



2. All components dissolved, free concentrations of some components given

Constant pH: Complexes of Hg(II) with hydroxide and chloride (ex04.mat)

What is the distribution of mercury species in a solution with 10^{-9} M Hg(II), 0.1M Cl^- and pH 8.3 ?

Choose Hg++, Cl-, and H+ as components and put up the matrix:

	Hg++ ***total***	**Cl-** ***total***	**H+** ***free***	
Hg++	1	0	0	0
HgOH+	1	0	-1	-3.4
Hg(OH)2	1	0	-2	-6.2
Hg(OH)3-	1	0	-3	-21.1
Hg2OH+++	2	0	-1	-3.3
HgCl+	1	1	0	6.72
HgCl2	1	2	0	13.23
HgCl3-	1	3	0	14.2
HgCl4-2	1	4	0	15.3
Cl-	0	1	0	0
OH-	0	0	-1	-14
H+	0	0	1	0
	1e-9	**0.1**	**5e-9**	

Constant p_{CO_2}: Equilibrium of a soda solution with atmospheric CO_2 (ex05.mat)

10^{-4} moles of soda (Na_2CO_3) are dissolved in one liter of water. A certain pH establishes immediately. If this solution is left open to the atmosphere it will take up CO_2 from the air, and the pH will decrease until a new equilibrium is reached. What is this pH, and how much atmospheric CO_2 is taken up by this solution?

Solution: The solution gives up CO_2 until equilibrium with the atmosphere is reached. If one CO_3^{2-} turns into CO_2, two equivalent OH^- remain in the solution according to the reaction:

$$CO_3^{2-} + H_2O \leftrightarrow CO_2 + 2OH^-$$

The final solution therefore corresponds to a solution of $2 \cdot 10^{-4}$ M base that equilibrates with the atmosphere. This is represented by the following matrix:

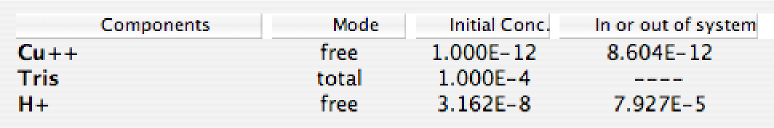
	CO2(g) ***free***	**OH-** ***total***	
H2CO3	1	0	-1.4
HCO3-	1	1	6.3
CO3--	1	2	10
H+	0	-1	-14
OH-	0	1	0
	3.5e-4	**2e-4**	

Constant free concentration of a species: Metal buffer for $Cu^{2+}_{(aq)}$ (ex06.mat)

What is the total conc of Cu(II) in a metal buffer with a free Cu^{2+} concentration of 10^{-12} M, a Tris concentration (Tris(hydroxymethyl)aminomethane) of 10^{-4} M at pH 7.5?

	Cu++ ***free***	**Tris** ***total***	**H+** ***free***	
Cu++	1	0	0	0
CuOH+	1	0	-1	-8
Cu(OH)2	1	0	-2	-15.2
Cu(OH)3-	1	0	-3	-26.8
Cu(OH)4--	1	0	-4	-39.9
Cu2(OH)2++	2	0	-2	-11
CuTris++	1	1	0	3.95
Cu(Tris)2++	1	2	0	7.63
Cu(Tris)3++	1	3	0	11.1
Cu(Tris)4++	1	4	0	14.1
CuOHTris+	1	1	-1	-2.05
(CuOHTris)2++	2	2	-2	1.9
CuOH(Tris)2+	1	2	-1	1.31
Cu(OH)2(Tris)2	1	2	-2	-6.59
Tris	0	1	0	0
HTris+	0	1	1	8.09
OH-	0	0	-1	-14
H+	0	0	1	0
	1e-12	**1e-4**	**3e-8**	

The total concentration of copper can be read from the bottom part of the data window as the sum of the 'free conc.' and the amount that had to be added in order to provide the desired equilibrium situation, 'in or out of system'. -> $Cu_{tot} = 9.60 \cdot 10^{-12}$ M



Components	Mode	Initial Conc.	In or out of system
Cu++	free	1.000E-12	8.604E-12
Tris	total	1.000E-4	----
H+	free	3.162E-8	7.927E-5

3. Dissolution of one (or more) solid phase(s)

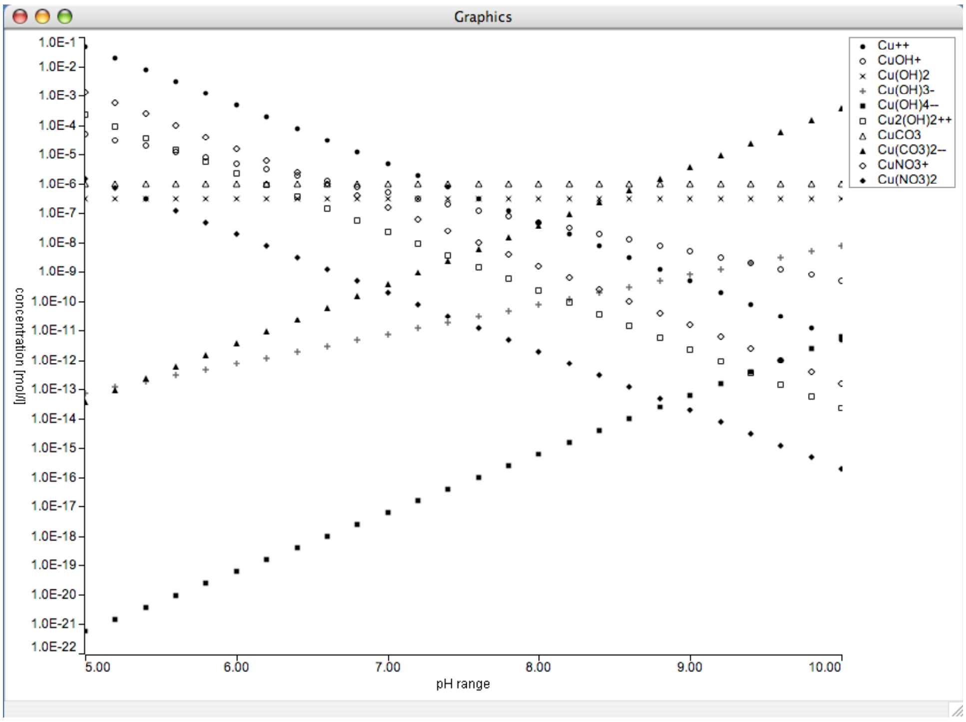
Dissolution diagram of $Cu(OH)_{2(s)}$ (ex07.mat)

Calculate the maximum soluble copper in the pH range between 5 and 10 (log conc. vs. pH) if $Cu(OH)_2$ is the limiting phase! Use complexes of Cu(II) with hydroxide, carbonate and nitrate in pure water in equilibrium with atmospheric p_{CO2} of $5 \cdot 10^{-4}$ atm which contains 0.01 M NO_3^-:

Compile a matrix consisting of NO3-, Cu++, CO2 and H+, then replace Cu++ with Cu(OH)2(s) using ***Insert Solid Phase...***

	NO3-	**Cu(OH)2**	**CO2**	**H+**	
	total	***solidPhase***	***free***	***free***	
Cu++	0	1	0	2	8.68
CuOH+	0	1	0	1	0.68
Cu(OH)2	0	1	0	0	-6.52
Cu(OH)3-	0	1	0	-1	-18.12
Cu(OH)4--	0	1	0	-2	-31.22
Cu2(OH)2++	0	2	0	2	6.36
CuCO3	0	1	1	0	-2.72
Cu(CO3)2--	0	1	1	-2	-16.83
CuNO3+	1	1	0	2	9.18
Cu(NO3)2	2	1	0	2	8.28
NO3-	1	0	0	0	0
H2CO3	0	0	1	0	-1.5
HCO3-	0	0	1	-1	-7.82
CO3--	0	0	1	-2	-18.15
OH-	0	0	0	-1	-14
H+	0	0	0	1	0
	1e-2	**1**	**5e-4**	**1e-7**	

To calculate speciation for a pH range, choose *pH range* in the *Options* menu, enter the desired range and step size (e.g. pH 5 to 10 in steps of 0.2 pH units). A logarithmic representation of the Cu species looks as follows:


Graphics
1.0E-1
1.0E-2
1.0E-3
1.0E-4
1.0E-5
1.0E-6
1.0E-7
1.0E-8
1.0E-9
1.0E-10
1.0E-11
1.0E-12
1.0E-13
1.0E-14
1.0E-15
1.0E-16
1.0E-17
1.0E-18
1.0E-19
1.0E-20
1.0E-21
1.0E-22
concentration [mol/l]
5.00
6.00
7.00
8.00
9.00
10.00
pH range
● Cu++
○ CuOH+
× Cu(OH)2
+ Cu(OH)3-
■ Cu(OH)4--
□ Cu2(OH)2++
△ CuCO3
▲ Cu(CO3)2--
◇ CuNO3+
◆ Cu(NO3)2

The $CaCO_3$ – CO_2 system (ex08.mat)

What is the pH and composition of a water which is in equilibrium with calcite, $CaCO_3$ and atmospheric p_{CO_2} ($10^{-3.5}$ atm) ? How much CO_2 and $CaCO_3$ dissolve in one liter of pure water?

	CaCO3	**CO2**	**H+**	
	solidPhase	***free***	***total***	
Ca++	1	-1	2	9.7
CaOH+	1	-1	1	-2.5
CaCO3(aq)	1	0	0	-5.3
CaHCO3+	1	0	1	3.3
H2CO3	0	1	0	-1.5
HCO3-	0	1	-1	-7.8
CO3--	0	1	-2	-18
OH-	0	0	-1	-14
H+	0	0	1	0
	1.0	**3.16e-4**	**0**	

pH is 8.265, $4.834\cdot10^{-4}$ mol Calcite and $4.757\cdot10^{-4}$ mol CO_2 dissolve in the solution until equilibrium is reached.

Dissolution of $Ca_4Al_2O_6SO_4 \cdot 12H_2O$ (ex09.mat)

If $Ca_4Al_2O_6SO_4 \cdot 12H_2O$ dissolves congruently, stoichiometric amounts of Ca(II) and Al(III) are released. What are the concentrations of totally dissolved Ca(II) and Al(III), and what is the pH of the solution?

	Ca4Al2O6SO4 ***solidPhase***	**Al+++** ***total***	**SO4--** ***total***	**H+** ***total***	
Ca++	0.25	-0.5	-0.25	3	18.6
CaOH+	0.25	-0.5	-0.25	2	5.75
Al+++	0	1	0	0	0
AlOH++	0	1	0	-1	-5
Al(OH)2+	0	1	0	-2	-9.3
Al(OH)3	0	1	0	-3	-15
Al(OH)4-	0	1	0	-4	-23
SO4--	0	0	1	0	0
OH-	0	0	0	-1	-14
H+	0	0	0	1	0
	1	**0**	**0**	**0**	

Note that start concentrations are zero for all components except the solid phase. From the data window you will find the total concentrations by addition of the respective species concentrations:

$Ca_{tot} = 4.14 \cdot 10^{-3}$ M, $Al_{tot} = 2.07 \cdot 10^{-3}$ M, and the pH = 11.59.

Dissolution of several solid phases (ex10.mat)

What is the pH and composition of a 10^{-2} M solution for NO_3^- which is in equilibrium with the carbonate phases of Zn(II), Cd(II), Pb(II), and Cu(II), and atmospheric p_{CO_2} ($10^{-3.5}$ atm) ? Which solid is the most soluble, which the least soluble?

	ZnCO3(s)	**CdCO3(s)**	**PbCO3(s)**	**CuCO3(s)**	**NO3**	**CO2(g)**	**H+**	**{log K}**
	solidPhase	*solidPhase*	*solidPhase*	*solidPhase*	*total*	*free*	*total*	
Zn++	1	0	0	0	0	-1	2	7.98
ZnOH+	1	0	0	0	0	-1	1	-0.98
Zn(OH)2	1	0	0	0	0	-1	0	-8.92
Zn(OH)3-	1	0	0	0	0	-1	-1	-20.42
Zn(OH)4--	1	0	0	0	0	-1	-2	-33.22
ZnCO3(aq)	1	0	0	0	0	0	0	-5.37
ZnNO3+	1	0	0	0	1	-1	2	8.38
Zn(NO3)2	1	0	0	0	2	-1	2	7.68
Cd++	0	1	0	0	0	-1	2	4.36
CdOH+	0	1	0	0	0	-1	1	-5.74
Cd(OH)2	0	1	0	0	0	-1	0	-16.04
Cd(OH)3-	0	1	0	0	0	-1	-1	-28.94
Cd(OH)4--	0	1	0	0	0	-1	-2	-43.04
CdCO3(aq)	0	1	0	0	0	0	0	-9.39
CdNO3+	0	1	0	0	1	-1	2	4.86
Cd(NO3)2	0	1	0	0	2	-1	2	4.56
Pb++	0	0	1	0	0	-1	2	4.97
PbOH+	0	0	1	0	0	-1	1	-2.73
Pb(OH)2	0	0	1	0	0	-1	0	-12.13
Pb(OH)3-	0	0	1	0	0	-1	-1	-23.13
PbCO3(aq)	0	0	1	0	0	0	0	-6.13
Pb(CO3)2--	0	0	1	0	0	1	-2	-23.03
PbNO3+	0	0	1	0	1	-1	2	6.14
Pb(NO3)2	0	0	1	0	2	-1	2	6.37
Cu++	0	0	0	1	0	-1	2	8.47
CuOH+	0	0	0	1	0	-1	1	0.47
Cu(OH)2	0	0	0	1	0	-1	0	-6.73
Cu(OH)3-	0	0	0	1	0	-1	-1	-18.33
Cu(OH)4--	0	0	0	1	0	-1	-2	-31.43
CuCO3(aq)	0	0	0	1	0	0	0	-2.88
Cu(CO3)2--	0	0	0	1	0	1	-2	-17.04
CuNO3+	0	0	0	1	1	-1	2	8.97
Cu(NO3)2	0	0	0	1	2	-1	2	8.07
H2CO3	0	0	0	0	0	1	0	-1.5
HCO3-	0	0	0	0	0	1	-1	-7.82
CO3--	0	0	0	0	0	1	-2	-18.15
NO3-	0	0	0	0	1	0	0	0
OH-	0	0	0	0	0	0	-1	-14
H+	0	0	0	0	0	0	1	0
	1	**1**	**1**	**1**	**0.01**	**5E-4**	**0**	

result: pH = 7.80, solubility: Cu > Zn > Pb > Cd

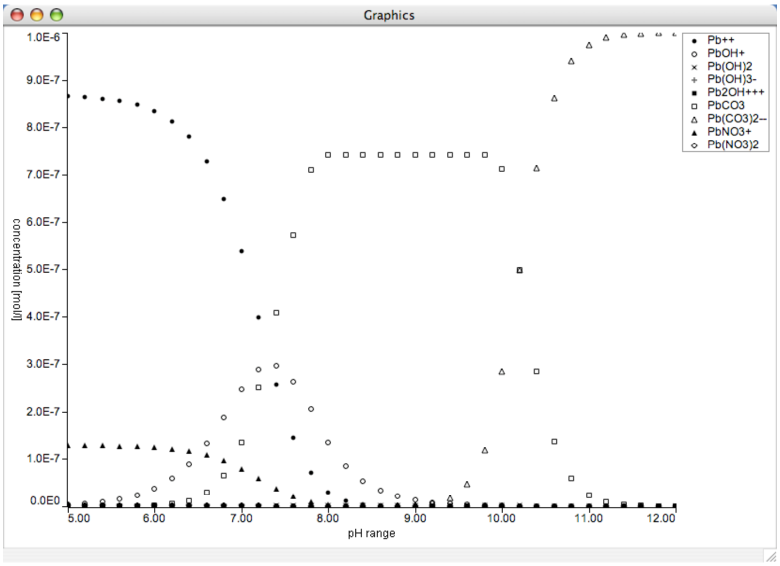
4. Precipitation of one (or more) solid phases

Precipitation of $PbCO_3(s)$ (ex11.mat)

Is a solution with 10^{-6} M Pb(II) oversaturated with respect to $PbCO_3(s)$ between pH 5 to 12 ? The solution contains 0.01M NO_3^- for ionic strength and is in equilibrium with CO_2 at $p_{CO2} = 10^{-3.5}$ atm.

	NO3-	**PbCO3**	**CO2**	**H+**	
	total	***checkPrecip***	***free***	***free***	
Pb++	0	1	-1	2	4.97
PbOH+	0	1	-1	1	-2.73
Pb(OH)2	0	1	-1	0	-12.13
Pb(OH)3-	0	1	-1	-1	-23.13
Pb2OH+++	0	2	-2	3	3.54
PbCO3(aq)	0	1	0	0	-6.13
Pb(CO3)2--	0	1	1	-2	-23.03
PbNO3+	1	1	-1	2	6.14
Pb(NO3)2	2	1	-1	2	6.37
NO3-	1	0	0	0	0
H2CO3	0	0	1	0	-1.5
HCO3-	0	0	1	-1	-7.82
CO3--	0	0	1	-2	-18.15
OH-	0	0	0	-1	-14
H+	0	0	0	1	0
	1e-2	**1e-6**	**3.16e-4**	**1e-4**	

Choose pH range and enter from 5 to 12 in steps of 0.2. A graphical representation of all Pb(II) species reveals that precipitation occurs between approx. pH 6 and 11:



5. Adsorption to particulate surfaces:

One particulate surface type

Surface speciation of γ-Al_2O_3 in 0.1M $NaClO_4$ at pH 7:

(According to the examples of *J. Westall*, using four adsorption models).

Constant Capacitance Model *(ex12.mat)*

	SOH adsorbent1	charge charge1.1	H+ free	
SO-	1	-1	-1	-9.24
SOH	1	0	0	0
SOH2+	1	1	1	7.4
OH-	0	0	-1	-13.8
H+	0	0	1	0
	1.0	**0.0**	**1e-7**	

ConstantCap	**{model}**
129	**{surface area in m^2/g}**
1.37e-4	**{no. of surface sites mol/g}**
8.174	**{conc. of solid in g/l}**
0.1	**{ionic strenght in M}**
1.06	**{inner capacitance in F/m^2}**

Diffuse Layer Model (ex13.mat)

```
             SOH        charge       H+
         adsorbent1charge1.1      free

SO-           1            -1         -1            -8.98
SOH           1             0          0                0
SOH2+         1             1          1             7.66
OH-           0             0         -1            -13.8
H+            0             0          1                0

              0            0.0       1e-7

Diffuse/GTL          {model}
129                  {surface area in m2/g}
1.28e-4              {no. of surface sites mol/g}
8.174                {conc. of solid in g/l}
0.1                  {ionic strenght in M}
```

Basic Stern Layer Model *(ex14.mat)*

	SOH	**1st ch.**	**2nd ch.**	**H+**	
	adsorbent1	***charge1.1***	***charge1.2***	***free***	
SO-	1	-1	0	-1	-8.46
SOH	1	0	0	0	0
SOH2+	1	1	0	1	8.16
OH-	0	0	0	-1	-13.8
H+	0	0	0	1	0
	0	**-1**	**-0.5**	**1e-7**	

SternL	**{model}**
129	**{surface area in m^2/g}**
1.33e-4	**{no. of surface sites mol/g}**
8.174	**{conc. of solid in g/l}**
0.1	**{ionic strenght in M}**
2.4	**{inner capacitance in F/m^2}**

Triple Layer Model *(ex15.mat)*

	SOH	**1st ch.**	**2nd ch.**	**3rd ch.**	**H+**	
	adsorbent1	***charge1.1***	***charge1.2***	***charge1.3***	***free***	
SO-Na+	1	-1	1	0	-1	-9.31
SOH2+ClO4-	1	1	-1	0	1	7.33
SO-	1	-1	0	0	-1	-9.31
SOH	1	0	0	0	0	0
SOH2+	1	1	0	0	1	7.33
OH-	0	0	0	0	-1	-13.8
H+	0	0	0	0	1	0
	0	**0**	**0**	**0**	**1e-7**	

TripleL	**{model}**
129	**{surface area in m^2/g}**
1.32e-4	**{no. of surface sites mol/g}**
8.174	**{conc. of solid in g/l}**
0.1	**{ionic strenght in M}**
1.2	**{inner capacitance in F/m^2}**
0.2	**{outer capacitance in F/m^2}**

Adsorption of Lead on Goethite *(ex16.mat)*

Pb^{2+} adsorbs on Goethite (α-FeOOH). In order to obtain surface complexation constants for Pb^{2+} we titrated a solution of $2.4 \cdot 10^{-7}$ mol/l Pb(II) with a goethite suspension at pH 7.15 at an ionic strength of 0.01M KNO_3 in a concentration range of 0-50 mg/l Goethite. Calculate the titration curve Pb_{ads} vs. Goethite! Use the Generalized Two Layer Model ("Diffuse/GTL"). The following parameters and constants were experimentally obtained:

specific surface :	14.7 m^2/g
H^+-exchange capacity :	$1.35 \cdot 10^{-4}$ mol/g

	Pb++	**FeOOH**	**charge**	**H+**	**{log K}**
	total	***adsorbent1***	***charge1.1***	***free***	
Pb++	1	0	0	0	0
PbOH+	1	0	0	-1	-7.7
Pb(OH)2	1	0	0	-2	-17.1
Pb(OH)3-	1	0	0	-3	-28.1
Pb2OH+3	2	0	0	-1	-6.4
FeOOPb+	1	1	1	-1	-0.52
(FeOO)2Pb	1	2	0	-2	-5.27
FeOOH2+	0	1	1	1	6.7
FeOOH	0	1	0	0	0
FeOO-	0	1	-1	-1	-9
OH-	0	0	0	-1	-14
H+	0	0	0	1	0
	2.4e-7	**1.0**	**0.0**	**7.08e-8**	

Diffuse/GTL	{model}
14.7	{surface area in m^2/g}
1.350e-4	{no. of surface sites mol/g}
1e-3	{conc. of solid in g/l}
0.01	{ionic strength in mol/l}

Choose ***Adsorption range...*** from the ***Options*** menu and enter the concentration range (dimension is g/l, therefore: from 0 to 0.05 in steps of e.g. 0.0025). Choose ***Graphics...*** and select the two surface species. A graphical representation of the titration curve will be calculated that shows the increasing formation of surface complexes, or inverse if you select dissolved Pb(II) species, the disappearing of Pb(II) from the solution.

Two or more (up to five) particulate surface types

Constant Capacitance Model ***(ex17.mat)***

	AxOH	**Ch1**	**BxOH**	**Ch2**	**CxOH**	**Ch3**	**H+**	
	adsorbent1		***adsorbent2***		***adsorbent3***		***free***	
		charge1.1		***charge2.1***		***charge3.1***		
AxO-	1	-1	0	0	0	0	-1	-9.24
AxOH	1	0	0	0	0	0	0	0
AxOH2+	1	1	0	0	0	0	1	7.4
BxO-	0	0	1	-1	0	0	-1	-9.24
BxOH	0	0	1	0	0	0	0	0
BxOH2+	0	0	1	1	0	0	1	7.4
CxO-	0	0	0	0	1	-1	-1	-9.24
CxOH	0	0	0	0	1	0	0	0
CxOH2+	0	0	0	0	1	1	1	7.4
OH-	0	0	0	0	0	0	-1	-13.8
H+	1	0	1	0	0	0	1	0
	1	**0**	**1**	**0**	**1**	**0**	**1e-7**	

ConstantCap			**{model}**
129	129	129	**{area}**
1.37E-04	1.37E-04	1.37E-04	**{surface sites}**
8.174	8.174	8.174	**{solid conc}**
0.1			**{ionic strength}**
1.06	1.06	1.06	**{inner capacitance}**

Three identical particles (same as example ex12.mat - ex15.mat) were assumed for the demonstration of this program option.

Diffuse Layer Model / General Two Layer Model *(ex18.mat)*

	AOH	**chA**	**BOH**	**chB**	**COH**	**chC**	**H+**	
	adsorbent1	***charge1.1***	***adsorbent2***	***charge2.1***	***adsorbent3***	***charge3.1***	***free***	
AO-	1	-1	0	0	0	0	-1	-8.98
AOH	1	0	0	0	0	0	0	0
AOH2+	1	1	0	0	0	0	1	7.66
BO-	0	0	1	-1	0	0	-1	-8.98
BOH	0	0	1	0	0	0	0	0
BOH2+	0	0	1	1	0	0	1	7.66
CO-	0	0	0	0	1	-1	-1	-8.98
COH	0	0	0	0	1	0	0	0
COH2+	0	0	0	0	1	1	1	7.66
OH-	0	0	0	0	0	0	-1	-13.8
H+	0	0	0	0	0	0	1	0
	0.0	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**1E-7**	

Diffuse/GTL			**{model}**
129	129	129	**{surface area}**
1.28E-04	1.28E-04	1.28E-04	**{sites conc}**
8.174	8.174	8.174	**{conc in g/l}**
0.1			**{ionic strength}**

Basic Stern Layer Model *(ex19.mat)*

```
                AOH ChA1 ChA2 BOH1ChB1ChB2 COH ChC1ChC2  H+

             adsorbent1 charge1.2  charge2.1 adsorbent3 charge3.2
                  charge1.1 adsorbent2 charge2.2  charge3.1      free

AO-             1    -1    0    0    0    0    0    -1    0    -1       -8.46
AOH             1     0    0    0    0    0    0     0    0     0           0
AOH2+           1     1    0    0    0    0    0     0    0     1        8.16

BO-             0     0    0    1   -1    0    0     0    0    -1       -8.46
BOH             0     0    0    1    0    0    0     0    0     0           0
BOH2+           0     0    0    1    1    0    0     0    0     1        8.16

CO-             0     0    0    0    0    0    1    -1    0    -1       -8.46
COH             0     0    0    0    0    0    1     0    0     0           0
COH2+           0     0    0    0    0    0    1     1    0     1        8.16

OH-             0     0    0    0    0    0    0     0    0    -1       -13.8
H+              0     0    0    0    0    0    0     0    0     1           0

               0.0   0.0  0.0  0.0  0.0  0.0  0.0   0.0  0.0  1E-7

SternL                                       {model}
129         129         129                  {spec. surface m2/g}
1.33E-04    1.33E-04    1.33E-04             {sites conc. in mol/g}
8.174       8.174       8.174                {conc. in g/l}
0.1                                          {ionic strength}
2.4         2.4         2.4                  {inner capacitance F/m2}
```

Triple Layer Model *(ex20.mat)*

	AxOH	**ChA1**	**ChA2**	**ChA3**	**BxOH**	**ChB1**	**ChB2**	**ChB3**	**CxOH**	**ChC1**	**ChC2**	**Ch3**	**H+**	
	adsorbent1	***charge1.1***	***charge1.2***	***charge1.3***	***adsorbent2***	***charge2.1***	***charge2.2***	***charge2.3***	***adsorbent3***	***charge2.3c***	***charge2.3***	***harge2.3***	***free***	
AxO-Na+	1	-1	1	0	0	0	0	0	0	0	0	0	-1	-9.31
AxOH2+ClO4-	1	1	-1	0	0	0	0	0	0	0	0	0	1	7.33
AxO-	1	-1	0	0	0	0	0	0	0	0	0	0	-1	-9.31
AxOH	1	0	0	0	0	0	0	0	0	0	0	0	0	0
AxOH2+	1	1	0	0	0	0	0	0	0	0	0	0	1	7.33
BxO-Na+	0	0	0	0	1	-1	1	0	0	0	0	0	-1	-9.31
BxOH2+ClO4-	0	0	0	0	1	1	-1	0	0	0	0	0	1	7.33
BxO-	0	0	0	0	1	-1	0	0	0	0	0	0	-1	-9.31
BxOH	0	0	0	0	1	0	0	0	0	0	0	0	0	0
BxOH2+	0	0	0	0	1	1	0	0	0	0	0	0	1	7.33
CxO-Na+	0	0	0	0	0	0	0	0	1	-1	1	0	-1	-9.31
CxOH2+ClO4-	0	0	0	0	0	0	0	0	1	1	-1	0	1	7.33
CxO-	0	0	0	0	0	0	0	0	1	-1	0	0	-1	-9.31
CxOH	0	0	0	0	0	0	0	0	1	0	0	0	0	0
CxOH2+	0	0	0	0	0	0	0	0	1	1	0	0	1	7.33
OH-	0	0	0	0	0	0	0	0	0	0	0	0	-1	-13.8
H+	1	0	0	0	0	0	0	0	0	0	0	0	1	0
	0	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**1e-7**	

TripleL			**{model}**
129	129	129	**{area}**
1.32E-04	1.32E-04	1.32E-04	**{surface sites}**
8.174	8.174	8.174	**{solid conc}**
0.1			**{ionic strength}**
1.2	1.2	1.2	**{inner capacitance}**
0.2	0.2	0.2	**{outer capacitance}**

Several types of surface sites on one type of particle

(Maximum: three different site types and five different particles)

Diffuse Layer Model / General Two Layer Model (ex21.mat)

	strongSites	**weakSites**	**charge**	**M++**	**H+**	
	adsorbent1.1	***adsorbent1.2***	***charge1.1***	***total***	***free***	
strong=SO-	1	0	-1	0	-1	-8.98
strong=SOH	1	0	0	0	0	0
strong=SOH2+	1	0	1	0	1	7.66
weak=SO-	0	1	-1	0	-1	-8.98
weak=SOH	0	1	0	0	0	0
weak=SOH2+	0	1	1	0	1	7.66
strong=SOM+	1	0	1	1	-1	-7
weak=SOM+	0	1	1	1	-1	-9
M++	0	0	0	1	0	0
OH-	0	0	0	0	-1	-13.8
H+	0	0	0	0	1	0
	0.0	**0.0**	**0.0**	**1.0E-6**	**1.0E-7**	

Diffuse/GTL		**{model}**
129	129	**{surface area in m^2/g}**
1.28E-04	2.56E-04	**{conc. of surface sites, mol/g}**
8.174	8.174	**{solid conc. in g/l}**
0.1		**{ionic strength in mol/l}**

6. pε-pH diagrams

The S(VI), S(0), S(-II) - System (ex22.mat)

fig. 7.5. (Stumm and Morgan, Aquatic Chemistry, 1981)

	SO4-- ***total***	**e-** ***free***	**H+** ***free***	
SO4--	1	0	0	0
HSO4-	1	0	1	2
S(s)	1	6	8	36.2
H2S	1	8	10	41
HS-	1	8	9	34
e-	0	1	0	0
OH-	0	0	-1	-14
H+	0	0	1	0
	1E-2	**1E+5**	**1E-7**	

Choose ***pX-pY-diagram*** from the ***Options*** menu and fill in the window:

For a reasonnable range select '**H+**' as X-component in the pX range **0 to 11**

Select '**e-**' as Y-component in the pY range **-10 to +10**.

The **Step Size** can be set to eg. **0.5**, otherwise the calculation takes much time.

The **Main Comp.**that the species of interest are derived from is **SO4--**, and there are the first **5** species to plot.

The Chlorine System (ex23.mat)

fig. 7.6. (Stumm and Morgan, Aquatic Chemistry, 1981)

	Cl- *total*	e- *free*	H+ *free*	
Cl-	1	0	0	0
Cl2(aq)	2	-2	0	-47.2
HOCl	1	-2	-1	-50.5
OCl-	1	-2	-2	-57.8
e-	0	1	0	0
OH-	0	0	-1	-14
H+	0	0	1	0
	0.04	**1E-20**	**1E-5**	

Choose **pX-pY-diagram** from the **Options** menu and fill in the window:

For a good range select '**H+**' as X-component in the pX range **-2 to 10**

Select '**e-**' as Y-component in the pY range **20 to 30**.

The **Step Size** can be set to e.g. **0.5**, otherwise the calculation takes much time.

The **Main Comp.** that the species of interest are derived from is **Cl-**, and there are the first **4** species to plot.

7. Solubility diagrams

The Iron - CO_2 System *(ex24.mat)*

fig. 7.9. (Sigg und Stumm, Aquatische Chemie, 1995, 3dr ed.)

	Fe++	**HCO3-**	**HS-**	**H+**	
	total	***total***	***total***	***free***	
Fe++	1	0	0	0	0
FeCO3(s)	1	1	0	-1	0.4
Fe(OH)2(s)	1	0	0	-2	-12.9
FeS(s)	1	0	1	-1	4.2
H2CO3	0	1	0	1	6.3
HCO3-	0	1	0	0	0
CO3--	0	1	0	-1	-10.3
H2S	0	0	1	1	7
HS-	0	0	1	0	0
S--	0	0	1	-1	-19
OH-	0	0	0	-1	-14
H+	0	0	0	1	0
	1E-6	**5E-3**	**1E-9**	**1E-7**	

Choose **pX-pY-diagram** from the **Options** menu and fill in the window:

For a reasonnable range select '**H+**' as X-component in the pX range **5 to 14**

Select '**HS-**' as Y-component in the pY range **0 to +10**.

The **Step Size** can be set to a larger number, eg. **0.5**

The **Main Comp.**that the species of interest are derived from is **Fe++**, and there are the first **4** species to plot.

The $PbCO_3$ - $PbSO_4$ system (ex25.mat)

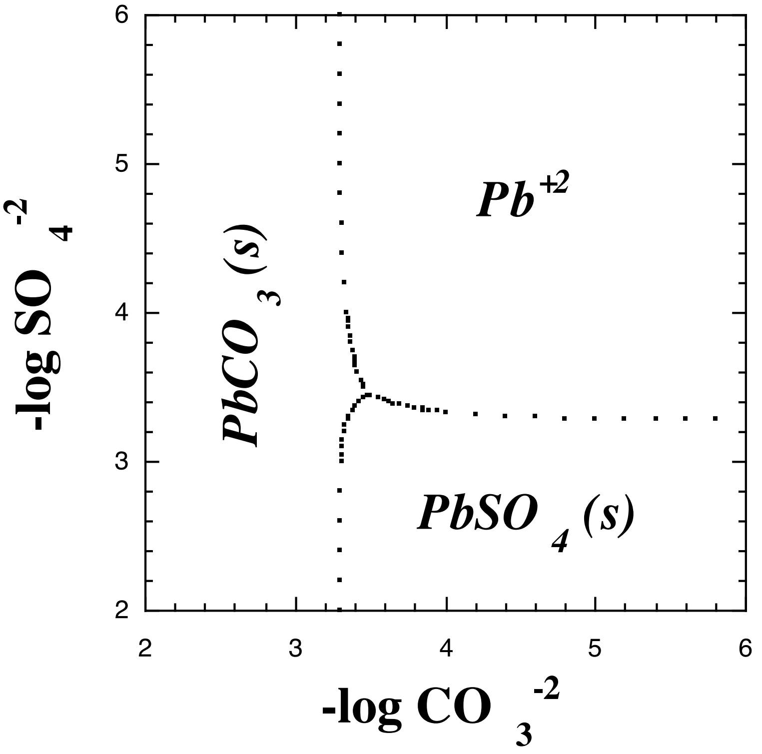
Which solid, $PbCO_3$ or $PbSO_4$, precipitates in a system with lead and various concentrations of carbonate and sulfate?

Select a matrix with the components Pb++, SO4--, CO3--, and H+ from the library.

Save and move to EXCEL. Add the formation equations for the two solids **PbCO3 (s)** and **PbSO4 (s)** to the matrix. All together there are now 15 Pb-species:

	Pb++ *total*	**CO3-- *total***	**SO4-- *total***	**H+ *total***		
PbCO3(s)	1	1	0	0	13.13	
PbSO4(s)	1	0	1	0	7.79	
Pb++	1	0	0	0	0	
PbOH+	1	0	0	-1	-7.7	25,0 S&M
Pb(OH)2	1	0	0	-2	-17.1	25,0 S&M
Pb(OH)3-	1	0	0	-3	-28.1	25,0 S&M
Pb2OH+++	2	0	0	-1	-6.4	25,0 S&M
Pb3(OH)4++	3	0	0	-4	-23.9	25,0 S&M
Pb4(OH)4++++	4	0	0	-4	-20.9	25,0 S&M
Pb6(OH)8++++	6	0	0	-8	-43.6	25,0 S&M
PbHCO3+	1	1	0	1	13.5	
PbCO3	1	1	0	0	6.33	
Pb(CO3)2--	1	2	0	0	9.66	
PbSO4(aq)	1	0	1	0	2.75	25,0 S&M
Pb(SO4)2--	1	0	2	0	1.99	25,1 S&M
H2CO3	0	1	0	2	16.68	25,0 S&M
HCO3-	0	1	0	1	10.33	25,0 S&M
CO3--	0	1	0	0	0	
SO4--	0	0	1	0	0	
HSO4-	0	0	1	1	1.99	25,0 S&M
OH-	0	0	0	-1	-14	
H+	0	0	0	1	0	
	1E-3	**1E-3**	**1E-3**	**0.0**		

The following graph can be calculated with ***pX-pY Diagram*** from the ***Options*** menu. Select CO3-- and SO4-- as X and Y and enter the concentration range:


6
5
4
3
2
2
3
4
5
6
-log SO_4^{-2}
-log CO_3^{-2}
$PbCO_3(s)$
Pb^{+2}
$PbSO_4(s)$