

Practical 1: Modelling Aqueous Solutions with PHREEQC

1. Calculate the solubility of anhydrite as a function of temperature. Set up the phreeqc file with vi or some other text editor..

```
TITLE Solubility of anhydrite
SOLUTION 1
      units      mol/kgw
      pH         4.00
      temp       300.0
EQUILIBRIUM_PHASES
Anhydrite
END
```

Note that temperature in PHREEQC is input in °C. Edit the input file to cover a range of temperatures from 25 to 300 °C. USE THE Inl.dat DATABASE FILE SINCE THAT HAS THE Cp INFO etc.

In the output, you'll find

```
-----Distribution of species-----
Species Molality      Log      Log      Log
          Activity    Molality Activity    Gamma
H+       2.790e-05     2.685e-05  -4.554  -4.571  -0.017
OH-      2.010e-07     1.932e-07  -6.697  -6.714  -0.017
H2O      5.553e+01     1.000e+00   1.744  -0.000   0.000
Ca       9.391e-05
Ca+2     7.637e-05     6.531e-05  -4.117  -4.185  -0.068
CaSO4    1.753e-05     1.753e-05  -4.756  -4.756   0.000
CaOH+    3.575e-13     3.436e-13 -12.447 -12.464  -0.017
```

The "solubility of anhydrite" can be taken as the concentration of Ca. The line

```
Ca           9.391e-05
```

means that the total Ca concentration is 9.39×10^{-5} molal. Anhydrite has a "retrograde solubility". What might that mean?

2. Calculate the solubility (i.e., total Ag in solution) of AgCl (chlorargyrite) as a function of [Cl] (0.0 to 0.2 m) and temperature (25-300°C) using PHREEQC. To do this, set up the input file:

```
TITLE Solubility of AgCl
SOLUTION 1
      units      mol/kgw
      pH         4.00
      temp       25.0
      Na         0.20 charge
      Cl         0.20
EQUILIBRIUM_PHASES
Chlorargyrite 0.0 1.0
END
```

In this input, the block SOLUTION 1 sets up the initial solution (saltwater). The second block, EQUILIBRIUM_PHASES, requires that there be a target saturation index for Chlorargyrite to be 0.0 (i.e., at saturation) but says we have a total of 1.0 moles of AgCl per kg of water (which ought to be enough to prevent it from all dissolving...).

Edit the file to change the temperature and [Na] and [Cl] as you wish..

In the output file (if all goes well..) you'll find, near the end, the speciation of Ag under the block

```
-----Distribution of species-----
```

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	9.915e-05	8.935e-05	-4.004	-4.049	-0.045
OH-	6.500e-08	5.805e-08	-7.187	-7.236	-0.049
H2O	5.553e+01	9.999e-01	1.744	-0.000	0.000
Ag(1)	6.843e-03				
AgCl	4.538e-03	4.538e-03	-2.343	-2.343	0.000
Ag+	1.774e-03	1.581e-03	-2.751	-2.801	-0.050
AgCl2-	5.305e-04	4.742e-04	-3.275	-3.324	-0.049
AgCl3-2	9.005e-08	5.749e-08	-7.046	-7.240	-0.195
AgCl4-3	3.899e-11	1.420e-11	-10.409	-10.848	-0.439

The line

Ag (1) 6.843e-03

tells us the total Ag concentration is 6.843×10^{-3} molal; the lines below give us the molality etc. of the different complexes. Use the "lnl.dat" database as that has the Cp and H data we need to do the calculation up to 300 °C. Run the calculation for a number of temperatures and NaCl concentrations. Make sure that $[Na]=[Cl]$ for charge balance. Plot your results in a nice way for publication..

3. Calculate the pH of seawater as function of pCO_2 in the atmosphere given that seawater is saturated in calcite. The PHREEQC input file is

```
TITLE pH of seawater after equilibration with atmosphere..
SOLUTION 1 SEAWATER FROM NORDSTROM ET AL. (1979)
  units      ppm
  pH         8.22
  pe         8.451
  density    1.023
  temp       25.0
  redox      O(0)/O(-2)
  Ca         412.3
  Mg         1291.8
  Na         10768.0
  K          399.1
  Fe         0.002
  Mn         0.0002  pe
  Si         4.28
  Cl         19353.0
  S(6)       2712.0
  N(5)       0.29    gfw    62.0
  N(-3)      0.03    as     NH4
  O(0)       1.0     O2(g) -0.7
EQUILIBRIUM_PHASES
  CO2(g) -3.5 1000.
  Calcite
```

END

The third line from the bottom means that we are requiring SOLUTION 1 to equilibrate with an infinite reservoir of $CO_2(g)$ at partial pressure of $10^{-3.5}$ bar. Change that line for each run...