Geochemical Modelling

Physics and Chemistry of Minerals and Solutions
University of Bristol

Objectives of Geochemical Modelling..

- Predict the solubilities of chemical components.
- Predict change in solution composition after mineral-water reactions..
- Predict mineral stabilities.

Method..

- Define the unique ("basis") species that define the composition (i.e., the components).
- Consider all of the species that might form from that basis.
- Set up the mass-action law for each species.
- Set up the mass or charge balance constraint.
- Solve the simultaneous equations...

Example: ZnS in 0.1m NaCl, pH = 3

- Define a set of "basis" species (components) that define the compositional variations of the system:

Zn^{+2}, H_2S, Cl^-, H^+, Na^+

- Consider all of the other species that might form from that basis:

$ZnS(s) + H^+ = Zn^{+2} + HS^-$

$Zn^{+2} + Cl^- = ZnCl^-$

$Zn^{+2} + 2Cl^- = ZnCl_2^-$

$HS^- + H^+ = H_2S$

(Note: each equilibrium must be unique so that one reaction cannot be a sum of two others.)

Example: Solubility of ZnS

•Write mass action expressions for each species:

$$\frac{[Zn^{+2}][HS^{-}]}{[H^{+}]} = 10^{-1.46}$$

$$\frac{[H^{+}][HS^{-}]}{[H_2S]} = 10-?$$

$$\frac{[ZnCl^{+}]}{[Zn^{+2}][Cl^{-}]} = 10^{-6.3}$$

$$\frac{[ZnCl_2]}{[Zn^{+2}][Cl^{-}]^2} = 10^{-10.33}$$

Example: Solubility of ZnS

•Write mass conservation for each component

Cl_{tot} = [Cl-] + [$ZnCl^{+}$] + 2[$ZnCl_2^{-}$] = 0.1 m

Na_{tot} = [Na^{+}] = 0.1 m

[H^{+}] = 10^{-3}

Write charge conservation:

2[Zn^{+2}] + [H+] + [$ZnCl^{+}$] + [Na^{+}]

= [Cl-] + [HS^{-}] + [$ZnCl_2^{-}$]

Example: Solubility of ZnS

We have 8 unknowns and 8 equations. However, the equations are non-linear!

Moreover, we are ignoring the activity coefficients which cannot be determined until we know the concentrations of all the charged species.

But these cannot be determined until we know the activity coefficients..!

Popular Computer Programs

- PHREEQC (U.S. Geological Survey)
- MINTEQ (US EPA)
- Geochemist's Workbench (University of Illinois)
- EQ3 (Lawrence Livermore National Lab)

ZnS solubility using PHREEQC

Here is the input file for our problem:

```
TITLE ZnS solubility on 0.1 m NaCl
SOLUTION
pH 3.0
units mol/kgw
Na 0.1
Cl 0.1
EQUILIBRIUM_PHASES
Sphalerite 0.0 1.0
END
```

We have two blocks: one (SOLUTION) to specify the initial solution composition and the other (EQUILIBRIUM_PHASES) to constrain which phases will be present.

ZnS solubility using PHREEQC

The output file for our problem contains the total dissolved Zn and the speciation of Zn:

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
Zn	9.439e-06				
Zn+2	8.815e-06	3.560e-06	-5.055	-5.449	-0.394
ZnCl+	5.798e-07	4.501e-07	-6.237	-6.347	-0.110
ZnCl2	3.956e-08	3.956e-08	-7.403	-7.403	0.000
ZnCl4-2	2.656e-09	9.377e-10	-8.576	-9.028	-0.452
ZnCl3-	2.118e-09	1.644e-09	-8.674	-8.784	-0.110

So, we find that total dissolved zinc is 9.4×10^{-6} m (0.61 ppm) and that most of the Zn is uncomplexed by Cl- (e.g., as $Zn(H_2O)_6^{+2}$).

ZnS solubility using PHREEQC

Our calculation uses a thermodynamic "database" which contains *log K* and *ΔH* for different complex formation and mineral dissolution reactions:

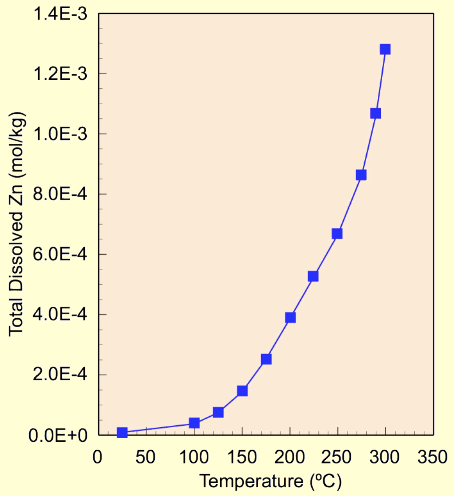
```
SOLUTION_SPECIES
1.0000 Zn++ + 1.0000 Cl-   =  ZnCl+
        -llnl_gamma           4.0
        log_k           +0.1986
        -delta_H        43.317  kJ/mol
-analytic 1.1235e+002 4.4461e-002 -4.1662e+003 -4.5023e+001 -
6.5042e+001
#       -Range:  0-300
PHASES
Sphalerite
    ZnS +1.0000 H+   =  + 1.0000 HS- + 1.0000 Zn++
    log_k       -11.4400
    -delta_H     35.5222 kJ/mol   # Enthalpy
    -analytic -1.5497e+002 -4.8953e-002 1.7850e+003 6.1472e+001
2.7899e+001
#       -Range:  0-300
```

ZnS solubility using PHREEQC

If there is are ΔH values for all our species/minerals, we can calculate solubilities at temperatures other than that of the default of 25 ºC:

```
TITLE ZnS solubility on 0.1 m NaCl
SOLUTION
pH 3.0
Temp 250
units mol/kgw
Na 0.1
Cl 0.1
EQUILIBRIUM_PHASES
Sphalerite 0.0 1.0
END
```

ZnS solubility using PHREEQC



Repeating the calculation for a number of different temperatures we can see how the solubility of ZnS changes with T. Note the slope changes…

Batch Reaction Model Example

Input bulk chemistry (PHREEQC)..

This is the water analysis in spring associated with china clay pits (Cornwall)..

```
TITLE China Clay Spring
SOLUTION
        units mg/L
        density 1.000
        pH 6.5
        temp    25.0
        Si 4
        Al 0.05
        K 4
END
```

We want to determine if this water is in equilibrium with the altered granite.

Batch Reaction Model Example (Cont.)

First, PHREEQC solves for the solution speciation:

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

                                                      Log       Log         Log
          Species             Molality    Activity  Molality  Activity     Gamma

          H+                 3.189e-07   3.162e-07    -6.496    -6.500    -0.004
          OH-                3.192e-08   3.166e-08    -7.496    -7.500    -0.004
          H2O                5.551e+01   1.000e+00     0.000     0.000     0.000
Al               1.853e-06
          Al(OH)4-           1.202e-06   1.192e-06    -5.920    -5.924    -0.004
          Al(OH)2+           4.328e-07   4.292e-07    -6.364    -6.367    -0.004
          Al(OH)3            2.000e-07   2.000e-07    -6.699    -6.699     0.000
          AlOH+2             1.791e-08   1.732e-08    -7.747    -7.762    -0.015
          Al+3               5.940e-10   5.513e-10    -9.226    -9.259    -0.032
H(0)             1.416e-24
          H2                 7.079e-25   7.079e-25   -24.150   -24.150     0.000
K                1.023e-04
          K+                 1.023e-04   1.014e-04    -3.990    -3.994    -0.004
          KOH                1.112e-12   1.112e-12   -11.954   -11.954     0.000
O(0)             0.000e+00
          O2                 0.000e+00   0.000e+00   -44.080   -44.080     0.000
Si               6.657e-05
          H4SiO4             6.654e-05   6.654e-05    -4.177    -4.177     0.000
          H3SiO4-            3.129e-08   3.103e-08    -7.505    -7.508    -0.004
          H2SiO4-2           6.902e-15   6.674e-15   -14.161   -14.176    -0.015
```

Batch Reaction Model Example (Cont.)

Next, PHREEQC calculates the the *saturation index* for each possible mineral:

$$S.I. = \log \frac{Q}{K}$$

```
-----------------------------Saturation indices------------------------------

          Phase               SI  log IAP   log KT

          Al(OH)3(a)       -0.56    10.24    10.80  Al(OH)3
          Chalcedony       -0.63    -4.18    -3.55  SiO2
          Gibbsite          2.13    10.24     8.11  Al(OH)3
          H2(g)           -21.00   -21.00     0.00  H2
          K-feldspar       -1.88     0.22     2.09  KAlSi3O8
          K-mica            8.00    20.70    12.70  KAl3Si3O10(OH)2
          Kaolinite         4.69    12.13     7.43  Al2Si2O5(OH)4
          O2(g)           -41.12    42.00    83.12  O2
          Quartz           -0.20    -4.18    -3.98  SiO2
          SiO2(a)          -1.47    -4.18    -2.71  SiO2
```

We are oversaturated (SI > 0) in several minerals; with time, they would precipitate out. However, it is more complicated than that..

Batch Reaction Model Example (Cont.)

Now we can let the solution equilibrate with K-feldspar and see what happens. We constrained the reaction so that K-mica is not allowed to precipitate out since that is kinetically slow..

----------------------------Phase assemblage-------------------------------

Phase	SI	log IAP	log KT	Moles in assemblage Initial	Final	Delta
K-feldspar	0.00	2.09	2.09	1.000e+01	1.000e+01	-1.107e-04
K-mica	4.20	16.90	12.70	0.000e+00		0.000e+00
Kaolinite	0.00	7.44	7.43	0.000e+00	5.550e-05	5.550e-05

The solution will react with K-feldspar to produce kaolinite..

Batch Reaction Model Example (Cont.)

Solution composition after reacting with feldspar..

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

	Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
	OH-	2.725e-05	2.685e-05	-4.565	-4.571	-0.006
	H+	3.782e-10	3.728e-10	-9.422	-9.429	-0.006
	H2O	5.551e+01	1.000e+00	0.000	0.000	0.000
Al	1.497e-06					
	Al(OH)4-	1.497e-06	1.475e-06	-5.825	-5.831	-0.006
	Al(OH)3	2.917e-10	2.917e-10	-9.535	-9.535	0.000
	Al(OH)2+	7.491e-13	7.381e-13	-12.125	-12.132	-0.006
	AlOH+2	3.723e-17	3.511e-17	-16.429	-16.455	-0.026
	Al+3	1.500e-21	1.318e-21	-20.824	-20.880	-0.056
H(0)	2.023e-30					
	H2	1.012e-30	1.012e-30	-29.995	-29.995	0.000
K	2.130e-04					
	K+	2.129e-04	2.098e-04	-3.672	-3.678	-0.006
	KOH	1.952e-09	1.952e-09	-8.710	-8.710	0.000
O(0)	8.147e-33					
	O2	4.074e-33	4.074e-33	-32.390	-32.390	0.000
Si	2.875e-04					
	H4SiO4	2.052e-04	2.052e-04	-3.688	-3.688	0.000
	H3SiO4-	8.235e-05	8.115e-05	-4.084	-4.091	-0.006
	H2SiO4-2	1.570e-08	1.481e-08	-7.804	-7.830	-0.026

Summary

•Mass-action constraint to relate different species (simultaneous equilibria).

•Mass conservation constraint.

•We solve simultaneous non-linear equations.

•Kinetic effects can be accounted for by imposing undersaturation or oversaturation..