Solubility Equilibria and Solid Solutions

Physical Chemistry of Minerals and Solutions
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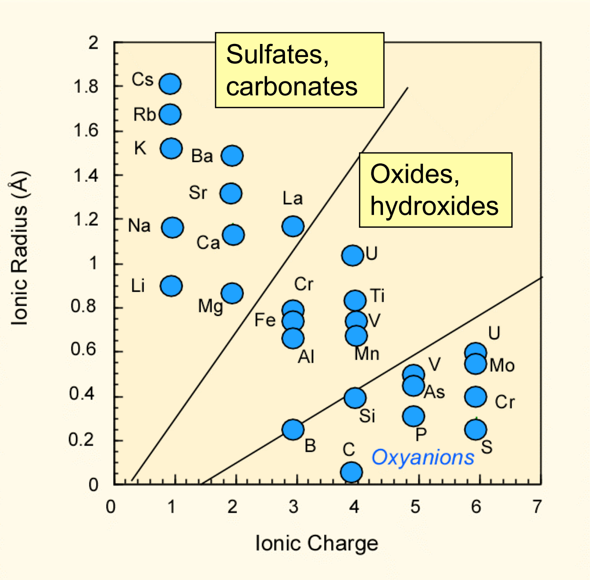
Geochemical Motivation

•Solubility equilibria control the major element compositions of natural waters.

•Several important kinds of sedimentary rock are precipitates from aqueous solutions (e.g., carbonates, evaporites).

•Many important kinds of ore-deposits result from precipitation from hydrothermal and diagenetic solutions.

Ionic Potential and Aqueous Chemistry



Congruent vs. Incongruent Dissolution

Congruent dissolution (all products are soluble):

(i) $CaSO_4(s) = Ca^{2+} + SO_4^{2-}$

(ii) $CaCO_3(s) = Ca^{2+} + CO_3^{2-}$

Incongruent dissolution (new solids form):

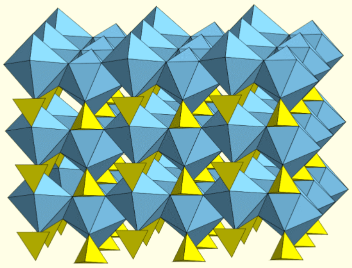
(i) $2KAlSi_3O_8(s) + 2H_2O =$

$Al_2Si_2O_5(OH)_4(s) + 2K^+ + 2OH^-$

(ii) $KFe_3(SO_4)_2(OH)_6\,(s) + 3H_2O\ =$

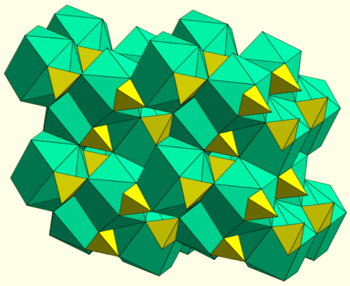
$K^+ + 3Fe(OH)_3(s) + 2SO_4^{2-} + 3\,H^+$

Sulfate Mineral Structures



Anhydrite ($CaSO_4$) structure

Barite ($BaSO_4$) structure



Discrete SO_4^{2-} and M^{2+} ions held together by ionic bonds..

Solubility of Sulfate Minerals

Mineral	**Solubility Equilibrium**	**pK**
Anhydrite	$CaSO_4 = Ca^{+2} + SO_4^{-2}$	4.2
Celestite	$SrSO_4 = Sr^{+2} + SO_4^{-2}$	6.6
Anglesite	$PbSO_4 = Pb^{+2} + SO_4^{-2}$	7.7
Barite	$BaSO_4 = Ba^{+2} + SO_4^{-2}$	10.0

If (and only if) the solution is in equilibrium with solid MSO_4:

$$K = \frac{a_M a_{SO_4}}{a_{MSO_4}} \approx [M^{2+}][SO_4^{-2}]$$

=1 if pure phase

Saturation, Unsaturation and Supersaturation

Consider the dissolution of $CaSO_4 = Ca^{2+} + SO_4^{-2}$:

•A solution will be ***saturated*** in a solid $CaSO_4$ if that solid is present. The ion product $[Ca][SO_4] = K$.

•A solution will be ***unsaturated*** if solid $CaSO_4$ is absent and $[Ca][SO_4] < K$.

•A solution will be ***supersaturated*** if $CaSO_4$ is absent and $[Ca][SO_4] > K$.

•The ***saturation index*** $Q = \log([Ca][SO_4]/K)$.

Simple Solubility Calculations

Example: Calculate the concentration of Pb in a solution saturated with $PbSO_4$. pK for $PbSO_4$ is 7.7.

Solution: $PbSO_4$ dissolves according to

$$PbSO_4 = Pb^{2+} + SO_4^{2-}$$

With $K = [Pb][SO_4] = 2 \times 10^{-7}$. If no other species are present, then, by charge balance we have

$$[Pb] = [SO_4] = x$$

Hence, $x^2 = K$ so that $x = [Pb] = 1.4 \times 10^{-4}$ moles/liter.

Simple Solubility Calculations (Cont.)

We can convert to ppm (mg/kg) as follows: Since the atomic mass of Pb is 207.2 g/mole, we have

$$\frac{1.4 \times 10^{-4} \text{ moles Pb}}{\text{liter } H_2O} \times \frac{207.2 \text{ g Pb}}{\text{mole P}b} \times \frac{1 \text{ liter } H_2O}{\text{kg } H_2O} \times \frac{1000 \text{ mg}}{\text{g}}$$

$$= 29.3 \text{ mg Pb/kg } H_2O$$

The Common Ion Effect

Example: Calculate the solubility of Pb in a solution saturated with $CaSO_4$. pK for $PbSO_4$ is 7.7 while pK for $CaSO_4$ is 4.2.

We have two equilibria:

$$CaSO_4 = Ca^{2+} + SO_4^{2-}$$

with K_1 =[Ca][SO_4] = 6.3 x 10^{-5}, and

$$PbSO_4 = Pb^{2+} + SO_4^{2-}$$

with K_2 =[Pb][SO_4] = 2 x 10^{-8} . By charge balance we have

$$[Ca] + [Pb] = [SO_4]$$

The Common Ion Effect

But since $CaSO_4$ is much more soluble $PbSO_4$,

$[Ca] >> [Pb]$ or $[Ca] + [Pb] = [Ca]$.

Hence,

$[Ca] = [SO_4] = x$

Since

$K_1 = [Ca][SO_4] = 6.3 \times 10^{-5}$

we get

$[SO_4] = 7.9 \times 10^{-3}$

Now $K_2 = [Pb][SO_4] = 2.0 \times 10^{-8}$

$[Pb](7.9 \times 10^{-3}) = 2.0 \times 10^{-8}$

The Common Ion Effect (Cont.)

Or

$[Pb] = 2.5 \times 10^{-6}$ moles/liter.

Note how the solubility of $PbSO_4$ is much lower in the presence of $CaSO_4$.

The presence of minerals such as $CaCO_3$ and $CaSO_4$ can suppress the solubility of metals such as Pb and Cd via the ***common ion effect.***

Solubility Equilibria and PHREEQC

```
TITLE Solubility of CaSO4
SOLUTION
     units    mol/kgw
     pH       9.00
     temp     25.0
EQUILBRIUM_PHASES
     Gypsum 0.0 1.0
END
```

Saturation Index of gypsum

Moles of gypsum per kg of water

This is a simple example that will calculate the composition of a solution that is saturated in anhydrite.

Solubility and Solid Solutions

When an ion can be incorporated into a mineral by isomorphic substitution (solid solution), the aqueous solubility of the ion is greatly decreased.

We calculated the solubility of $PbSO_4$ to be [Pb] = 1.4 x 10^{-4} moles/liter. In the presence of $CaSO_4$, this decreased to 2.5 x 10^{-6} moles/liter due to the common ion effect.

If $PbSO_4$ is in solid solution with $CaSO_4$ then the activity of $PbSO_4$ solid will no longer be 1. Assuming ideal solid solution, we have

$$a_{PbSO_4} = X_{PbSO_4}$$

Solubility and Solid Solutions (Cont.)

Example: Calculate the solubility of $PbSO_4$ when it is in solid solution with $CaSO_4$ with X_{PbSO4} = 0.001.

Solution: Our solubility product expression will now be

$$K = \frac{[Pb][SO_4]}{a_{PbSO_4}} = \frac{[Pb][SO_4]}{X_{PbSO_4}} = 2.0 \times 10^{-8}$$

$[SO_4^{2-}]$ will be determined by the solubility of $CaSO_4$ to give $[SO_4] = 7.9 \times 10^{-3}$ moles/liter. Hence,

$[Pb] = 3.0 \times 10^{-9}$ moles/liter

Solid Solutions in PHREEQC

An ideal solution treatment for $CaSO_4$-$SrSO_4$-$BaSO_4$:

```
TITLE sstest
SOLID_SOLUTIONS 1
CaSrBaSO4
-comp Anhydrite 1.5
-comp Celestite 0.05
-comp Barite 0.05
SOLUTION 1
        units   mol/kgw
        pH      9.00
        temp    25.0
END
```

Non-Ideal Solutions

In a ***non-ideal*** solution, there is an excess free energy of mixing:

$$G_{mix} = X_A\mu_A + X_B\mu_B + G_{ex}$$

The excess free energy per mole of component

$$\overline{G}_1^{ex} = RT\ln\gamma_1$$

$$\overline{G}_2^{ex} = RT\ln\gamma_2$$

Non-Ideal Solutions: Margules Model

The ***Margules model*** attempts to express the excess free energy as (for a binary solution):

$$\overline{G}_{ex} = X_1(W_2X_1X_2) + X_2(W_1X_1X_2)$$

$$RT\ln\gamma_1 = (2W_2 - W_1)X_2^2 + 2(W_1 - W_2)X_2^2$$

$$RT\ln\gamma_2 = (2W_1 - W_2)X_1^2 + 2(W_2 - W_1)X_1^2$$

Non-Ideal Solutions: Margules Model

The ***dimensionless interaction parameters*** are simply

$$a_1 = W_1 / RT \quad a_2 = W_2 / RT$$

In PHREEQC, these are called non-dimensional Guggenheim parameters.

```
-Gugg_nondim   5.08       1.90
```

Example: Calcite-Dolomite

```
SOLID_SOLUTIONS 1
     Ca(x)Mg(1-x)CO3    # Binary, nonideal
     -comp1    Calcite          0.097
     -comp2    Ca.5Mg.5CO3      0.003
     -temp     25.0
     -Gugg_nondim   5.08        1.90
```

Non-Ideal Solutions: Regular Solution Model

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

In a ***non-ideal regular solution model***, we assume that

$$\Delta S_{mix} = \Delta S_{mix}(ideal)$$

but that

$$\Delta H_{mix} \neq 0$$

i.e., we are assuming that there is no excess vibrational entropy of mixing.

Symmetric Regular Solutions

For a ***symmetric*** regular solution

$$a_1 = a_2 = \lambda$$

So that,

$$\ln\gamma_1 = \lambda X_2^2$$

$$\ln\gamma_2 = \lambda X_1^2$$

This model is good for sulfate and carbonate minerals.

Symmetric Regular Solutions

Example, calcite-magnesite solid solution:

```
SOLID_SOLUTIONS 1
        Ca(x)Mg(1-x)CO3
                -comp1   Calcite     0.00
                -comp2   Magnesite   0.00
                -Gugg_nondim 3.7 0.0
```

Regular, Symmetric Solution Model

In a regular, symmetric solution, the enthalpy of mixing as

$$\Delta H_{mix} = \lambda X_A X_B = \lambda X_A (1 - X_A)$$

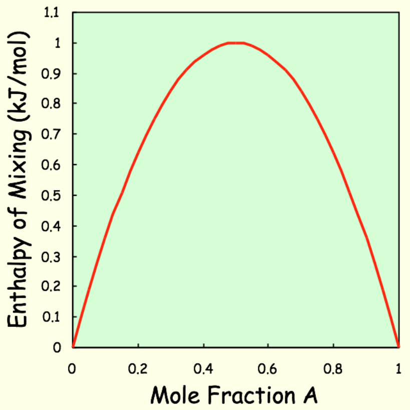
Then for a simple binary solution (e.g., (A,B)O):

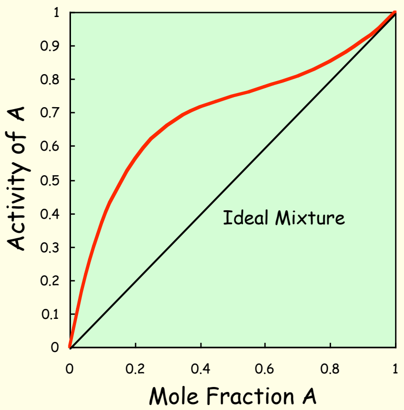
$$\mu_A = \mu_A^0 + RT \ln X_A + \lambda (1 - X_A)^2$$

$$a_A = X_A \exp\left(\frac{\lambda (1 - X_A)^2}{RT} \right)$$

Non-Ideal Solutions: Regular Solution Model

Example for λ=4 kJ/mol at 298 K:





Example: Cr in Jarosite

(Baron and Palmer, 2002)

$KFe_3(SO_4)_2(OH)_6$-$KFe_3(CrO_4)_2(OH)_6$

$$\Delta G_{ex} = X_{Cr} X_S RT a_0$$

With a_0 = -4.9 +/- 0.8

Example: Mg in Calcite

(Baron and Palmer, 2002)

$KFe_3(SO_4)_2(OH)_6$-$KFe_3(CrO_4)_2(OH)_6$

$$\Delta G_{ex} = X_{Cr} X_S RTa_0$$

With a_0 = -4.9 +/- 0.8

The Phase Rule

$$\boxed{f = c - p + 2}$$

•A ***phase*** is something that can be mechanically separated from the other phases (e.g., ice, water).

•A ***component*** is one of the smallest number of chemical species needed to define the compositions of the phases in the system (e.g., H_2O).

•A ***degree of freedom*** is a property that can be independently varied (e.g., P, T).

The Phase Rule

Example: the system $Ca^{2+} + CO_3^{-2} + H_2O + H^+$

Calcite ($CaCO_3$) + Aqueous solution + CO_2(g)

C = 4; p = 3 so f = 3. (e.g., P,T, pCO_2, pH)

Example: SiO_2 (qtz) + H_4SiO_4(aq) + Aqueous solution

C = 2; p = 2 so f = 2 (e.g., P,T, [H_2SiO_4])

Summary

•+2 and +3 cations can form insoluble carbonates, sulfates, sulfides and hydroxides.

•Solubility expression (congruent vs. incongruent).

•pH dependence of hydroxide, sulfide and carbonate solubilities.

•Common ion effect.

•Effect of solid solution.

•Complexing of metals by ligands will enhance solubility.

•Phase Rule