Lecture 9 Chemical Equilibrium and Speciation

(1) Supersaturated solutions:
   (a) have more dissolved substances than predicted by solubility alone
   (b) prevent the spontaneous crystallization of dissolved chemicals
   (c) have much less dissolved substance than predicted by solubility
   (d) a and b but not c

(2) One way we can get the equilibrium constant for a reaction we are interested in is to combine other reactions for which we know the constants. Show how this is done by deriving the equilibrium constant for the reaction of calcite with Mg\(^{2+}\) to form the CaMg-carbonate mineral called dolomite as written below:

\[
2\text{CaCO}_3(s) + \text{Mg}^{2+} = \text{CaMg(CO}_3\text{)}_2(s) + \text{Ca}^{2+}
\]

This is an important reaction used to describe the conversion of limestone to dolomite rock over geological time frames.

Combine (by addition or subtraction as necessary) the \(K_{eq}\) values for the following reactions (for 25°C) to get the \(K_{eq}\) (at 25°C) for the reaction of CaCO\(_3\) with Mg\(^{2+}\) to form dolomite as given above and derive an equation that expresses \(K_{eq}\) in terms of the Ksp listed above.

\[
\begin{align*}
\text{CaCO}_3(s) & = \text{Ca}^{2+} + \text{CO}_3^{2-} & \log K_{sp} = -8.48 \\
\text{CaMg(CO}_3\text{)}_2(s) & = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-} & \log K_{sp} = -16.70 \\
2\text{CaCO}_3(s) + \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-} & = 2\text{Ca}^{2+} + 2\text{CO}_3^{2-} + \text{CaMg(CO}_3\text{)}_2(s) & \\
(2 \times -8.48) + (+16.70) & = -0.26
\end{align*}
\]

(3) The equilibrium constant for this reaction can also be calculated from the values of free energy of formation. From thermodynamic data tables (Stumm and Morgan, 1981) we obtain the following standard free energies of formation at 25°C.

a) Calculate the standard free energy of reaction (\(\Delta Gr\))

\[
\begin{align*}
\text{Substance} & & \Delta G_f (\text{kJ mol}^{-1}) \\
\text{CaCO}_3(\text{calcite}) & & -1128.8 \\
\text{CaMg(CO}_3\text{)}_2(\text{dolomite}) & & -2161.7 \\
\text{Ca}^{2+} & & -553.54 \\
\text{Mg}^{2+} & & -454.8
\end{align*}
\]

\[
2\text{CaCO}_3 + \text{Mg}^{2+} = \text{CaMg(CO}_3\text{)}_2 + \text{Ca}^{2+} \quad \Delta G^r = \Sigma \Delta G^f \text{products} - \Sigma \Delta G^f \text{reactants} \\
(-553.54 + -2161.7) - (2(-1128.8) + -454.8) = -2.84
\]

\[
\log K = -\Delta Gr / 5.708 = -(-2.84)/5.708 = 0.497
\]
(4) The breakdown of the silicate mineral Ca-feldspar (also called anorthite) to form kaolinite clay is an important weathering reaction, particularly in humid climate soils. The reaction may be written:
\[
\text{CaAlSi}_2\text{O}_8 + 2\text{H}^+ + \text{H}_2\text{O} = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{2+}
\]
Ca-feldspar          kaolinite

a). Calculate the equilibrium constant for this reaction given the following free energies of formation.

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔG° (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-feldspar</td>
<td>-4001.4</td>
</tr>
<tr>
<td>H⁺</td>
<td>0</td>
</tr>
<tr>
<td>H₂O(l)</td>
<td>-237.14</td>
</tr>
<tr>
<td>kaolinite</td>
<td>-3799.4</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>-553.54</td>
</tr>
</tbody>
</table>

\[\Delta G = (-3799.4 + -553.54) - (-4001.4 + -237.14) = -114.4\]
\[\log K = -\Delta G / 5.708 = 20.04\]
\[K = 10^{20.04} = 1.1 \times 10^{20}\]

b) Assuming that soil moisture contains concentrations of [Ca²⁺] = 2 x 10⁻⁴ mol/l, and behaves as an ideal solution (no activity corrections), at what pH would anorthite be in equilibrium with the kaolinite and, therefore not weather?

\[K = \frac{\text{Ca} + \text{kaloinite}}{\text{H}^+ + \text{anorthite}} = \frac{[\text{Ca}]}{[\text{H}^+]}
\]

\[H^+ = \frac{[\text{Ca}]}{K} = \left(2 \times 10^{-4}/1.1 \times 10^{20}\right)^{1/2} = 1.348 \times 10^{-12}\]
\[pH = -\log H^+ = 11.8\]

(5) Gypsum solubility is written as:
\[
\text{CaSO}_4\cdot2\text{H}_2\text{O}(s) = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}
\]

pK = 4.58; K = 10⁻⁴.⁵⁸ = 2.62 x 10⁻⁵

a) If we added gypsum to distilled water (with no other salts present) and let it come to equilibrium, what would the equilibrium concentration of total Ca be?

\[K_{sp} = [\text{Ca}^{2+}] \times [\text{SO}_4^{2-}]; \quad [\text{Ca}^{2+}] = [\text{SO}_4^{2-}]; \quad [\text{Ca}^{2+}] = K_{sp}/2 = 5.12 \times 10^{-3}\]

b) If the total sulfate concentration of seawater is 25.0 x 10⁻³ mol kg⁻¹, what would be the concentration of total Ca if gypsum was at solubility equilibrium? How does this compare with the actual concentration of seawater? Is seawater saturated with respect to gypsum?

Concentrations and activity coefficients for seawater are:
\[\text{Ca}^{2+} = 10.28 \times 10^{-3} \quad \gamma = 0.28; \quad \text{SO}_4^{2-} = 28.00 \times 10^{-3} \quad \gamma = 0.12\]

If the sulfate concentration is 25.0 x 10⁻³ mol kg⁻¹ and the seawater is at solubility equilibrium then the concentration of Ca²⁺ is:

\[K_{sp} = [\text{Ca}^{2+}]\gamma_{\text{Ca}} \times [\text{SO}_4^{2-}]\gamma_{\text{SO}_4} = [\text{Ca}] \times 0.28 \times 25.0 \times 10^{-3} \times 0.12 = 2.62 \times 10^{-3}\]
\[[\text{Ca}] = 31 \times 10^{-3} \quad \text{mol kg}^{-1}\]

The actual Ca concentration is less than that but the sulfate concentration in seawater is 28 x 10⁻³ mol kg⁻¹.

To calculate saturation we need to use the seawater concentrations and activity coefficients and compare to Ksp.

\[K_{sp} = [\text{Ca}^{2+}]\gamma_{\text{Ca}} \times [\text{SO}_4^{2-}]\gamma_{\text{SO}_4} = 10.28 \times 10^{-3} \times 0.28 \times 28.0 \times 10^{-3} \times 0.12 = 9.67 \times 10^{-6}\]

This is less than 2.62 x 10⁻³ so seawater is undersaturated.
(6) Calculate the solubility (K) of CO2 in seawater using the ΔGf values and the relation between ΔGr and K.

\[ \text{CO}_2 (g) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \ (aq) \]

\[ \Delta G_f \]

\[ \Delta G_r = (-623.2) - (-394.37 + -237.18) = 8.35 \]

\[ \log K = -8.35/5.708 = 1.46 \]

\[ K = 10^{1.46} = 29 \]

(7) One way we can get the equilibrium constant for a reaction we are interested in is to combine other reactions for which we know the constants. In anoxic water like the Black Sea dissolved iron can be present as either Fe(OH)2(s) or FeCO3(s).

Below are some needed reactions:

1. \( \text{FeCO}_3(s) = \text{Fe}^{2+} + \text{CO}_3^{2-} \)  \( \log K = -10.4 \)
2. \( \text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \)  \( \log K = -10.3 \)
3. \( \text{Fe(OH)}_2(s) = \text{Fe}^{2+} + 2\text{OH}^- \)  \( \log K = -14.5 \)
4. \( \text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \)  \( \log K = -14.0 \)

(a) Write the reaction and give the equilibrium constant for the solubility of Fe(OH)2(s) in terms of H+.

(b) Write the reaction and give the equilibrium constant for the conversion of FeCO3 to Fe(OH)2.

(c) In seawater at pH 8 with HCO3^- = 2.0 \times 10^{-3}M, which phase of iron is more stable. Ignore activity corrections.

(a) This could be expressed as reaction # 3 minus 2 x reaction # 4:

\[ \text{Fe(OH)}_2(s) = \text{Fe}^{2+} + 2\text{OH}^- \]

\[ 2\text{H}^+ + 2\text{OH}^- = 2\text{H}_2\text{O} \]

\[ \text{Fe(OH)}_2(s) + 2\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O} \]

\[ \log K = -14.5 - 2(-14) = 13.5 \]

(b) This could be expressed as reaction # 1 minus reaction # 3:

\[ \text{FeCO}_3(s) = \text{Fe}^{2+} + \text{CO}_3^{2-} \]

\[ \text{Fe}^{2+} + 2\text{OH}^- = \text{Fe(OH)}_2(s) \]

\[ \text{FeCO}_3(s) + 2\text{OH}^- = \text{CO}_3^{2-} + \text{Fe(OH)}_2(s) \]

\[ \log K = -10.4 - (-14.5) = 4.1 \]

(c) \[ \text{FeCO}_3(s) + 2\text{OH}^- = \text{CO}_3^{2-} + \text{Fe(OH)}_2(s) \]

\[ \text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^- \]

\[ \text{FeCO}_3(s) + 2\text{OH}^- + \text{H}^+ = \text{HCO}_3^- + \text{Fe(OH)}_2(s) \]

\[ \log K = 4.1 - (-10.3) = 14.4 \]

\[ K = 10^{14.4} \]

\[ \text{pH} = 8 \]

\[ \text{H}^+ = 10^{-8} \quad \text{OH}^- = 10^{-6} \]

\[ K = \frac{\text{HCO}_3^-}{[\text{H}^+][\text{OH}^-]^2} = 2.0 \times 10^{-3} / 10^{-8} \times 10^{-12} = 2 \times 10^{17} \]

\[ \log K = -\Delta G_r / 5.708; \quad \Delta G = -17.3 \times 5.708 = -98.74 \]

Since \( \Delta G < 0 \) for the reaction, Fe(OH)2(s) is more stable.
The precipitation and dissolution of CaCO₃ is one of the important solubility reactions in seawater. The reaction can be written as: CaCO₃(s) = Ca²⁺ + CO₃²⁻.

a) Calculate ΔGr for this reaction given the following ΔGf species:

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔGf (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃(s)</td>
<td>-1128.79</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>-553.58</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>-527.81</td>
</tr>
</tbody>
</table>

\[-(-553.58 + -527.81) - (-1128.79) = 47.4 \text{ kJ mol}^{-1}\]

b) Calculate the equilibrium constant for this solubility reaction at 25°C.

\[\log K = \frac{-\Delta Gr}{5.708} = \frac{-47.4}{5.708} = -8.3 \]

\[K = 5 \times 10^{-9}\]

[CO₃²⁻] in surface water is about 260 μM Ca is 10.28 mM, is the water at saturation with respect to CaCO₃?

\[K = [Ca] \times [CO₃²⁻] = 260 \times 10^{-6} \times 10.28 \times 10^{-3} = 2.67 \times 10^{-4}\]

\[2.67 \times 10^{-4} > 5 \times 10^{-9}\] surface water is supersaturated.

In deep water at 4,500 meters in the Pacific [CO₃²⁻] is about 80 μM; Ksp at 4°C and in-situ pressure is 10⁻⁵.₉₅; is the deep water at saturation with respect to CaCO₃?

\[K = [Ca] \times [CO₃²⁻] = 80 \times 10^{-6} \times 10.28 \times 10^{-3} = 0.822 \times 10^{-4}\]

\[0.822 \times 10^{-4} < 10^{-5.95}\] so deep waters in the Pacific are undersaturated.