

**CE4591 Environmental Engineering Chemical Processes, Fall 2008
Problem Set 6**

Due: Friday, 11/21 by 5 p.m.

Solutions will be posted on the Web. Problem sets will be graded for completeness, and one problem (selected at random) will be graded in detail. Each problem set contributes 2.5% towards your final grade. Remember that for problems done with MINEQL, you must print out and attach the header file so that I can see your input.

1. Problem 15.3 (p. 454) in the text. Realize that the CaCO_3 is added to pure water. Some CaCO_3 is added to pure water that is open to the atmosphere; not all of the solid dissolves and the equilibrium pH is 8.1. What is the solubility product for CaCO_3 ?

SOLUTION: The solubility product will be for the reaction:



and the solubility product will be defined as:

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

Thus, to find the solubility product, we need to know the activities of Ca^{2+} and CO_3^{2-} . Because it is an open system, the CO_2 activity can be calculated from the pH (8.1) and the $p\text{CO}_2$ in the atmosphere (370 μatm).

$$\begin{aligned} K_a &= (\text{H}_2\text{CO}_3^*/\text{CO}_2) = 10^{-3.5} \text{ (mole/L-ster)} \\ &\Rightarrow [\text{H}_2\text{CO}_3^*] = (10^{-7.6} \text{ (mole/L-ster)})(370 \times 10^{-6} \text{ atm}) = 1.2 \times 10^{-13} \\ K_{a1} &= (\text{HCO}_3^-/\text{H}^+)(\text{H}_2\text{CO}_3^*) \\ &\Rightarrow [\text{HCO}_3^-] = K_{a1} [\text{H}_2\text{CO}_3^*]/[\text{H}^+] = 6.7 \times 10^{-6} \text{ M} \\ K_{a2} &= (\text{CO}_3^{2-}/\text{H}^+)(\text{HCO}_3^-) \\ &\Rightarrow [\text{CO}_3^{2-}] = K_{a2} (\text{HCO}_3^-)/[\text{H}^+] = 3.85 \times 10^{-9} \text{ M} \end{aligned}$$

To obtain the Ca^{2+} activity, it is suggested that we use the charge balance equation:

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

If activity coefficients are ignored, all quantities (except $[\text{Ca}^{2+}]$) are known, so we can rearrange to solve for this unknown:

$$\begin{aligned} [\text{Ca}^{2+}] &= 1/2 ([\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+]) = 1/2 (10^{-5.9} + 6.7 \times 10^{-6} + 2(3.85 \times 10^{-9}) - 10^{-8.1}) \\ [\text{Ca}^{2+}] &= 4.0 \times 10^{-6} \text{ M} \end{aligned}$$

Continuing to ignore activity coefficients, the solubility product would be:

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = (4.0 \times 10^{-6})(3.85 \times 10^{-9}) = 1.54 \times 10^{-14} = 10^{-14.81}$$

This value is close to the solubility product for Dolomite ($10^{-15.2}$). This discrepancy arises in part because we ignored activity coefficients and thereby underestimated the Ca^{2+} concentration.

2. Problem 15.5 (p. 455) in the text. Use MINEQL. The mineral name for $\text{Mn}(\text{OH})_2$ is pyrochroite, and for MnCO_3 is rhodochrosite. Part C will require some thinking. Solubility diagrams can be generated directly in MINEQL or the data can be copied to the clipboard and pasted into Excel for graphing.

15.5A. Draw a solubility diagram for $[\text{Mn}^{2+}]$ as a function of pH if $\text{Mn}(\text{OH})_2$ controls the Mn solubility and MnCO_3 does not exist. Assume a total dissolved carbonate concentration of 2×10^{-3} M.

SOLUTION: This problem is easily solved using MINEQL. We must be sure that H_2O , H^+ , Mn^{2+} , and CO_3^{2-} are checked as components. The header file would contain:

MINEQL+ Header file for pyrochroite.mfn:

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K Morrison



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