1.76 Aquatic Chemistry 2005 – Problems Set #4

Out: Tuesday, November 1
Due: Tuesday, November 15

Covers Chapters 5 and 6

(Show your work)

Computers will be helpful for these problems.

Important concepts: mineral dissolution precipitation, aqueous inorganic complexation.

Problem 1.

a) Write a balanced chemical reaction for the weathering of K-feldspar (KAlSi$_3$O$_8$) to gibbsite (Al(OH)$_3$).

b) Rewrite the chemical reaction provided in book Example 10 (Chapter 5) for the weathering of albite to Na-Montmorillonite so that the reaction coefficients for Na$^+$ and H$^+$ are equal to 1.

c) What is the equilibrium constant for this reaction?

d) You have collected a groundwater sample flowing through rocks that contain albite and Na-Montmorillonite. Chemical analyses reveal the presence of 0.0001 M [H$_2$SiO$_3$]$^-$ and 0.01 M [Na$^+$]. What is the pH of this fluid if it has reached a state of thermodynamic equilibrium with the host rock? Ignore ionic strength effects.

e) You notice that the host rock also contains quartz. Rewrite the reaction from part (b) so that it contains the mineral quartz (SiO$_2$) instead of H$_2$SiO$_3$ and calculate a new equilibrium constant (Requisite thermodynamic data is in Table 5.4 of the book). Using this new reaction, calculate the pH of the fluid. What can you say about the saturation state of the fluid with respect to quartz based on your result?

Problem 2. Book problem 5.10 part a: Calculate the composition of a groundwater in equilibrium with P$_{CO_2} = 10^{-1.5}$ atm, calcite, albite, and kaolinite.

COMMENT: In this system, albite weathers to kaolinite until albite and kaolinite are both in equilibrium with the solution. This happens when H$_2$SiO$_3$ and Na$^+$, which are initially absent in solution, build up until they reach saturation (expressed by the weathering reaction in Table 5.4). Some dissolved Al also results from this process, but its concentration remains negligible.

HINT: You should end up with an equation that is best solved by trial and error, or by using a computer root finding algorithm. You can get a good first approximation of the solution pH by neglecting the effect of albite weathering and considering only calcite.
Problem 3.
When the groundwater in Problem 3 emerges from a spring and enters into contact with the atmosphere, it is initially oversaturated with CO$_2$. Why must this be the case? As CO$_2$ escapes, calcite becomes oversaturated and precipitates from solution. Discuss, using equations if possible, how you would expect the pH, alkalinity, and C$_T$ in this water to change as CO$_2$ is lost to the atmosphere and calcite is lost to the sediments. Calculate the final composition of this water (pH, alkalinity, [Ca$^{2+}$]) when equilibrium with the atmosphere and calcite is reached.

Problem 4. - All thermodynamic data necessary for this problem are in Table 5.4 of the book. Ignore ionic strength effects for this question.

a) Draw a logC-pH diagram showing the aqueous speciation of Fe(II) in a 10$^{-8}$ M [Fe$^{2+}$]$_T$ solution as a function of pH. Consider the species Fe$^{2+}$, FeOH$^+$, Fe(OH)$_2$, Fe(OH)$_3$, H$^+$, and OH$^-$. Do not consider precipitation of solids.

b) If Fe(OH)$_2$($s$) were allowed to precipitate, what is the critical pH (pH of first precipitation)? Add the stability field for Fe(OH)$_2$($s$) to your logC-pH diagram.

c) Hydrogen sulfide is added to the solution to attain a total concentration ([H$_2$S]$_T$) equal to 10$^{-5}$ M. What is the critical pH for FeS($s$)? Modify the diagram to show the stability field for FeS($s$).

d) Which mineral is more stable at pH values less than 12?

e) Recalculate the critical pH for Fe(OH)$_2$($s$) ignoring the formation of Fe(II) aqueous complexes. Does aqueous complexation increase or decrease the solubility of Fe(OH)$_2$($s$)?