Geology 560, Prof. Thomas Johnson, Fall 2003
Unit II: Chemical reactions: Guide Questions

Goals:
- Refresh your memory on the basics of chemical reactions
- Ponder the chaos that underlies chemical reactions; there’s a lot of violent vibration and movement of atoms that goes on “behind the scenes”.
- Develop a feel for what a chemical equilibrium is.
- Refresh your memory about the mathematical equations we use to describe equilibrium
- Use all of this to understand acids and bases in water.
- Develop tools for calculating equilibrium conditions for solids in equilibrium with solutions
- Learn about a common model used to account for the way in which the presence of abundant ions in solution affects our saturation calculations
- Consider the effects of ion pairs and complexes
- Apply all of this to equilibria between calcite and solutions
- Apply some of this toward weathering of feldspar

**Important**: Some of the questions below are NOT addressed in Faure; you should think about these questions using your own experience.

1. Chemical reactions and chaos in the microscopic world (no reading, just use your own experience and class discussion) Questions like these will not appear on exams; this is mainly to review basic chemical principles.
   a. What causes a chemical reaction to happen?
   b. How do atoms/ions move when they are dissolved in water?
   c. Are the motions of ions/atoms during reactions orderly or chaotic?
   d. Why do many chemical reactions NOT happen? For example, we expect that a large pile of NaCl will dissolve completely in a liter of water, but even a small pile of AgCl will not dissolve completely. Why?
   e. Is it completely true to say that a reaction (like dissolution of AgCl) does not happen at all or do all reactions happen a little, perhaps so little that we don’t notice?
   f. If a crystal appears to be neither dissolving nor growing, does that mean that the atoms on the crystal surface have stopped moving?
   g. We usually think of reactions having reactants and products (e.g., gasoline plus oxygen \( \rightarrow \) CO2 plus water plus energy). But is it true for all reactions that the forward reaction happens and the reverse reaction does not?
   h. Why does gasoline in contact with air not explode at room temperature?
   i. How does the rate of a chemical reaction change as temperature increases?

2. The systematics of reactions (Faure, pp. 110-114)
   a. If a chemical reaction
      (example: \( \text{Ag}^+ + \text{Cl}^- = \text{AgCl} \))
involves two ions colliding with each other, how does the reaction rate change if we double the concentration of one of the ions?

b. If a chemical reaction involves the combining of TWO of an ion:
(example: \( \text{Ba}^{2+} + 2\text{Cl}^- = \text{BaCl}_2 \))
how does the reaction rate change if we double the \( \text{Cl}^- \) concentration? Why?

c. Does the rate of a given reaction depend only on the concentrations of the involved ions or are they affected by other ions in solution?

d. What correction factor do we use to account for the fact that the reaction rates depend on the concentrations of other ions?

e. What is the difference between molar and molal?

3. Chemical Equilibria (Faure, pp. 110-114)

a. If we bring two things together and a reaction occurs, when and why does the reaction appear to us to be “done” (i.e., nothing happens any more).
   i. In the gasoline example above, it is done when …?
   ii. But what about NaCl dissolving in water? Is this the same?

b. What does the word equilibrium mean? Does it mean everything stops?

c. Think about the chemical equilibrium between \( \text{N}_2 \) gas in the air and \( \text{N}_2 \) dissolved in water in a beaker. Imagine starting with water that has no \( \text{N}_2 \) dissolved in it at the start. Imagine what happens to individual \( \text{N}_2 \)'s as they collide with the water surface. What controls the amount of \( \text{N}_2 \) dissolved in water in equilibrium with air?

d. Using the answers to 2a, 2b and 2c above, explain the law of mass action in general terms.

e. Why are concentrations sometimes squared in the law of mass action?

f. Why do activities, and not concentrations, appear in the law of mass action?

g. Do chemical reactions always reach equilibrium?

h. What does it mean if a reaction goes to completion?

i. How does an increase in temperature affect the chance that a reaction will reach equilibrium?

j. If a reaction reaches equilibrium, and then we change temperature, pressure, or some other intensive variable, is the system necessarily at equilibrium?

k. So then, is the equilibrium constant always constant or does it change with pressure and temperature?

l. How does a system, initially at equilibrium, respond to an increase in concentration of one of the reactants?

m. How does a system, initially at equilibrium, respond to an increase in pressure?

4. \( \text{H}^+ \) and acids. Protonation, deprotonation. (Faure. 114 – 121)

a. What is the name for the fragment left after the proton leaves the acetic acid? What terminology is used for acids, oxanions, and organic anions in general?
b. If we dissolve some HCl in water, how likely is it that a proton (H\(^+\)) will escape from it?

c. If we put one acetic acid molecule in water containing a high H\(^+\) concentration, how likely is it that the proton (H\(^+\)) will escape from it?

d. What is the likelihood that another proton will replace the first one if it does escape?

e. How can we calculate things like:
   
i. At what value of [H\(^+\)] is acetate 50% protonated?
   
ii. What is [H\(^+\)] if we dissolve acetate in water (1 mol/L)?
   
iii. What is the speciation of acetic acid as a function of [H\(^+\)]?

f. What other species give off protons in water like acetate does? Know the common ones.

g. Is it possible for a species to give off protons under basic conditions when [H\(^+\)] is very small and also attract protons under acidic conditions?

h. In pure water, what is [H\(^+\)] (mol/L)? What is [OH\(^-\)] (mol/L)?

i. In a solution with a high [H\(^+\)], is [OH\(^-\)] high or low? Quantitatively, how does [OH\(^-\)] relate to [H\(^+\)]?

j. Why is the pH scale so useful for us?

k. Why do we care about H\(^+\) ions so much anyway?

5. **Cations, bases and hydroxyls (Faure 119-124)**
   
a. Why do small 2+ and 3+ cations dissolved in water tend to form complexes with hydroxyls?

b. If we put one CaO molecule into water, what happens? Is it much different from putting Ca(OH)\(_2\) into water?


c. How does the speciation of cations such as Al\(^{3+}\), Fe\(^{3+}\), Mg\(^{2+}\), Fe\(^{2+}\), and Ni\(^{2+}\) vary with pH? How can the speciation be calculated?

d. How does this affect the solubility of these elements?

6. **Solubility of ferric ion and aluminum**
   
a. Specifically, how soluble are Al and ferric iron at circummneutral pH?

b. How strongly does their solubility change if we increase or decrease pH?

7. **Solubility of silica (Faure, 124-127)**
   
a. How does the concentration of H\(_4\)SiO\(_4\) (in equilibrium with amorphous silica) vary as a function of pH?

b. How does the speciation of silicic acid change as a function of pH?
   
   i. How can we use the mass action expressions to calculate the speciation?

   c. How does this affect the solubility quartz or amorphous silica as a function of pH?

8. **Solubility of Salts (Faure 10.1)**
   
a. In a mass action expression for equilibrium between a solid and a solution, what is the activity of the solid phase?

b. Why doesn’t the mass action equation contain a variable for the surface area of the solid?

   c. What does it mean when we say a solution is saturated with respect to a certain solid?
d. Undersaturated? Supersaturated?
e. What do we typically use to express the amount of supersaturation or undersaturation of a given solution with respect to a given solid?
f. What is the ion activity product (IAP or Q)?
g. If a solution is supersaturated with respect to a certain solid, does that solid always precipitate from the solution?
h. What is a metastable phase?
i. A solution reacts with two solids that both contain a given ion. Why do we often see one of the solids precipitate and the other dissolve?

9. Hydrolysis: What happens when we put ions into water and those ions grab H⁺ or OH⁻? (Faure 10.2)
   a. Why does addition of FeCl₃ to water create an acidic solution? What other salts also do this?
   b. Why does addition of Na₃PO₄ to water create a basic solution? What other salts also do this?

10. Activity Coefficients: How can we modify our mass action expressions to account for the effects of other ions in solution? (Faure 10.3)
   a. How are the following effects built into the Debye-Hückel equation that can be used to estimate activity coefficients?
      i. The general decrease in activity caused by the presence of other ions in solution.
      ii. The greater sensitivity of more highly charged ions to the presence of other ions in solution.
      iii. The greater sensitivity of ions with smaller effective radii to the presence of other ions in solution.
   b. What is the effective radius of an ion (in this context)?
   c. In general, how do activity coefficients change as the ionic strength increases?
   d. What happens at very high ionic strength, though?
   e. If we calculate the amount of supersaturation for a supersaturated solution using concentrations instead of activities, in which direction is the error? Toward greater supersaturation or less?

11. Complexes: How can we account for the possibility that ions will form pairs and clusters that are not taken into account in the Debye-Hückel model?
   a. What, in a very general sense, are the processes that form and decompose ion pairs in solution?
   b. Note that we have already dealt with this in our consideration of weak acids and bases, which form complexes with H⁺ or OH⁻.
   c. How do we calculate the abundance of complexes?
   d. Can we assume equilibrium for complexes?
   e. After we have calculated the abundance of complexes, how does this information get used in our calculations of saturation indices of solids?

12. Understand how the following enter into calculations of the saturation state of calcite (Faure, 10.4):
   a. K_{sp}
b. Speciation of the various carbonate ions
c. Other speciation reactions- complexes
d. Activity coefficients
e. pH
f. Temperature

13. Weathering of Feldspar (Faure 10.5, 10.6)

a. Which element present in potassium-rich feldspar is so insoluble that it forms a new solid immediately after the feldspar is dissolved?
b. Is H⁺ involved in the weathering reaction? Why?
c. Which ions are readily taken away by moving solutions?
d. If these ions are taken away rapidly (e.g., think rain forest), does the reaction approach equilibrium? Why or why not?
e. Under low-moisture conditions, is equilibrium more likely to be approached? Why?
f. If equilibrium with two solid phases (e.g., K-feldspar and kaolinite; or kaolinite and gibbsite) occurs, does this constrain the activities of silica, potassium ion, and hydrogen ion?
g. How can we create a graph that gives us a "map" of the zones of equilibrium with various solid phases occur, as a function of silica, potassium ion, and hydrogen ion activity?