Geology 560  
Unit II, Class 1: Chemical reactions

Goals:
• Motivate: Show how chemical reactions control many basic aspects of the earth’s behavior
• 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”.
• This chaos causes a tendency toward randomness
• Think about forward and reverse reaction rates

Reading: Faure, 9.1 to 9.2

Relevant reactions in the geochemical world:

1. CaCO₃ (s) + CO₂(g) + H₂O ⇌ Ca²⁺(aq) + 2HCO₃⁻(aq)
   a. Importance:
      i. Main weathering reaction for limestone
      ii. The earth’s oceans contains CaCO₃ sediments, this is one way the oceans can EITHER absorb excess CO₂ (greenhouse gas) OR release CO₂, to regulate climate
   b. Points to think about:
      i. We have 2 ways of looking at reactions.
         1. Sometimes they go to completion (i above)
         2. Sometimes they approach equilibrium (ii above)
      ii. Recall the notation we use for chemical reactions
      iii. Recall that it is a good idea to check and make sure the reaction balances (i.e., there’s no loss or gain of atoms or charge)

2. Olivine + Quartz ⇌ Orthopyroxene
   Mg₂SiO₄ + SiO₂ ⇌ 2MgSiO₃
   a. It’s not obvious which is “preferred”- left or right side.
   b. Experiments tell us that the right side is.
   c. So if quartz is added to the earth’s mantle, it will tend to react with olivine to make pyroxene.
   d. But what happens if there’s lots of Fe in the system? It would tend to substitute into the olivine or pyroxene. Would this change things so the left side becomes stable?
   e. We have computer software that can calculate such things for us
      i. Based on experiments, BUT….
      ii. The software can calculate results for any composition, not just the ones for which people have done experiments (interpolation, maybe even some extrapolation)
   a. Upper Mantle = Olivine, Pyroxene, Garnet at about 400 km
   b. Lower Mantle = Perovskite (dominantly MgSiO$_3$)+ other minerals)
   c. The 670 km jump in seismic velocity is thought be related to this difference in the arrangement of the atoms (i.e., different minerals are stable)
      i. http://www.mala.bc.ca/~earles/mantle-nov99.htm
   d. Controversy: Can subducted slabs penetrate through the 670 discontinuity?
      i. Subducted slabs have different temperature and composition than lower mantle
      ii. If they are less dense than the lower mantle, they won’t sink into it
      iii. Density depends on the transition to perovskite assemblage

**Introduction to reactions: Order and chaos**

1. Example: NaCl dissolving into water
   \[ \text{NaCl} \leftrightarrow \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)} \]

   Why does the salt dissolve into the water?
   - Do the water molecules pluck the Na$^+$ + Cl$^-$ ions from the surface of the crystal? Not really. They don’t have arms!
   - Clearly, the ions have to move. One student suggested “diffusion” is involved.

   \[ (\text{Na}^+) \quad (\text{mg/L}) \]
   Distance (cm)
   - Picture a beaker with high concentration on one side, low on the other.
• Now picture the number of Na\(^+\) ions arriving at point A due to random motion alone.
• Now picture the number of Na\(^+\) ions leaving from point A due to random motion alone.
• If you consider all the additions and losses, you should find that the concentration at point A will decrease.
• Concentration at point B will increase
• AND, there will be a NET movement of ions from the high concentration side to the low concentration side.

Main point: The ions don’t “know” they are moving from high concentration to low concentration. Ions are not intelligent! The purely random motions result in a Net transfer from high to low concentration.

Also: Note that there are always some atoms that randomly migrate against the net diffusion flux. If we put some radioactive Na\(^+\) ions on the low concentration side, we WILL see some of them migrate to the high concentration side. Again, they move randomly, and do not know they are migrating against the NET flux.

Also: The system starts out a little bit ordered in this case; the concentration is high on one side and low on the other (if the link to order/disorder doesn’t seem clear, ask me). As time goes on, this system evolves toward less order, and eventually, the most disordered arrangement (concentration equal everywhere) will be attained. Thus, this system is evolving to a higher entropy state.
• On the microscopic scale: Chaos. Vibration/random motion/Brownian motion at the atomic scale is the ONLY driver behind this. The ions do not know anything about entropy (purely a human construct).
• On the macroscopic scale: Predictability. We see a smooth evolution from the situation in the graph above to the final one where the concentration is the same everywhere.

3. Now back to the NaCl dissolving in water:
• How do you think random vibrations, like those in the diffusion case above, affect the surface of the NaCl crystal?
• If we increase random vibrations in the system, how does this influence the rate of dissolution?
• Do you think that all ions at the NaCl surface are vibrating in exactly the same way? Or is there some chaos there, too, a bit like pop corn popping?
• Picture the motion of ions/molecules as a Na\(^+\) ion breaks free from the crystal. Do you think it takes a bit of extra energy to cause this to occur? From where does that energy come?
  1. Think of the atoms as having a range of energies.
  2. Energies are quantized- think of the bonds between atoms vibrating
     ▪ some with the “ground state” energy
     ▪ some with higher energies
     ▪ distribution of these energies among bonds is “random”
• Does the dissolution reaction increase or decrease the entropy of the system?

4. Switch to AgCl for a moment. This salt is known for being “insoluble”.
• How can this be? The chemical formula is not very different from NaCl!
  o Maybe the bonds in the solid are stronger.
  o Maybe the Ag\(^+\) is not happy dissolved in water.
  o The key here is the RELATIVE stability of the two phases.
• Is it possible for something to be 100.0000% insoluble? In other words, can we expect that not even one Ag\(^+\) ion will escape from the crystal into the water?

5. Switch to Quartz for a moment. Quartz is somewhat soluble.
• If we put a pile of fine quartz crystals in water, what happens (if we wait a few hours, like we would do for an NaCl experiment)?
• Would you expect that the amount of energy needed to break an SiO\(_4\)\(^-\) group free from the crystal would be greater or less than that needed to get Na\(^+\) free from NaCl?
• Preview of kinetics. Rates are slow when the “activation energy”, the amount of energy needed to make a single molecule break free, is high.