12.009 Problem Set 3

Due Tuesday, 1 March 2011

1. *Equilibrium of CO_2 with the Oceans & Ocean Acidification*: In class we discussed how carbon dioxide $[\mathrm{CO_2}]$ leaves a volcano and ends up both in the atmosphere and in the ocean. If $[\mathrm{CO_2}]$ was not reactive in water then we could predict the concentration of $[\mathrm{CO_2}]$ in the water based solely on its concentration in the air through our knowledge of Henry's Law (cough, 5.111), assuming that we waited long enough for the system to reach equilibrium. Henry's law normally takes the following form:

$$[\mathrm{CO_2}]_{solution} = k_H p. \tag{1}$$

Here, $[\mathrm{CO_2}]$ is the concentration of carbon-dioxide in the solution, k_H is the Henry's law coefficient (a function of the chemical, solvent and temperature) and p is the partial pressure of carbon-dioxide in the gas phase. This works quite well for finding the amount of dissolved gas in a solution. Unfortunately for us, carbon dioxide is not inert in water and can take on multiple forms. Two reactions in the 'carbonate system' and their respective equilibrium constants are:

$$\mathrm{CO_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{HCO_3^-} + \mathrm{H^+}, \qquad K_1 = \frac{[\mathrm{HCO_3^-}][\mathrm{H^+}]}{[\mathrm{CO_2}][\mathrm{H_2O}]} \tag{2}$$

and

$$\mathrm{HCO_3^-} \rightleftharpoons \mathrm{CO_3^{2-}} + \mathrm{H^+}, \qquad K_2 = \frac{[\mathrm{CO_3^{2-}}][\mathrm{H^+}]}{[\mathrm{HCO_3^-}]}. \tag{3}$$

Another critical equation you will need is the dissociation of water:

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-}, \qquad K_w = \frac{[\mathrm{H^+}][\mathrm{OH^-}]}{[\mathrm{H_2O}]}. \tag{4}$$

Because carbon dioxide takes part in these reversible reactions the amount of carbon dioxide stored in the ocean is not $[\mathrm{CO_2}]$ but rather

$$[\mathrm{DIC}] = [\mathrm{CO_2}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}], \tag{5}$$

where DIC signifies total dissolved inorganic carbon.

   (a) Find the equation for [DIC] as a function of the carbon dioxide concentration, the various equilibrium constants and the hydrogen ion concentration $[\mathrm{H^+}]$. Do the same for $[\mathrm{HCO_3^-}]$ and $[\mathrm{CO_3^{2-}}]$.

   (b) Assume for the moment that all charged species are accounted for by the above equations (yes, acids and bases in the ocean blatantly destroy this assumption). Write the system of equations which completely defines this system (Hint: remember to enforce electric neutrality)

(c) To make the problem more tractable assume that the reaction described in equation (3) does not occur. In addition assume that $K_w \ll [HCO_3^-]$. This is a massively fictitious ocean which is rather acidic. However, the fundamental mechanism in this ocean is the same as the real ocean. Solve for the dissolved inorganic carbon concentration, [DIC], as a function of the carbon dioxide pressure, p, and all other relevant constants. Use this to show that the derivative of [DIC] with respect to the partial pressure of CO_2 takes the following form:

$$\frac{\partial[\text{DIC}]}{\partial p} = k_H + \frac{\sqrt{K_1 k_H}}{2} p^{-1/2}. \tag{6}$$

Interpret the two terms on the right hand side of equation (6). Under what conditions is each term important and what is their physical interpretation? What does this suggest about the ocean as a sink for carbon dioxide?

2. *Isotopic Keeling Curve*: In class we discussed the famous Keeling curve which shows how carbon dioxide levels in the atmosphere are not only increasing but oscillating at the same time. We've placed carbon dioxide data from three stations, Point Barrow, Alaska; Mauna Loa, Hawaii; and South Pole Antarctica on the class website. This data is included in a .mat file and contains three structures (`PointBarrow`, `MaunaLoa`, and `SouthPole`). To give you a sense of how the data is actually structured `SouthPole.CO2.t` is the year that the concentration data was taken and `SouthPole.CO2.v` is the data in ppm. The carbon-13 data is in the same form with `SouthPole.d13.t` being the time and `SouthPole.d13.v` the δ^{13}C of atmospheric CO_2.

   (a) Provide two different plots. On the first plot show how the carbon concentration varies in time for all three stations. On the second plot show how the stable isotope values change in time for all three stations.

   (b) What causes the carbon dioxide concentration to oscillate? In what way does the oscillation of the carbon isotope value support or refute your rationale?

   (c) In what ways do the amplitude and phase (i.e. relative timing) of the oscillations in both plots change between sampling sites? Provide a rational argument for why these changes might occur. If you get stuck, look at where these sites are on the globe for inspiration.

   (d) Despite changes in the oscillations between each site, the general trend seems to be fairly constant. What is the general trend for concentration and isotopic value and why do you think it remains consistent between sites?

3. *Photons in the Sun*: This problem was inspired by an Encyclopedia Britannica article. We seek to answer the question: How long does it take for a photon generated by the fusion of hydrogen in the middle of the sun take to escape into the solar system? On the surface this seems like a straightforward question. All we need to do is divide the radius of the sun (7×10^8 meters) by the speed of light (3×10^8 meters/second) to get $\sim$2.6 seconds. This would be correct except for the fact that a photon travels approximately 0.1 cm before it is scattered in a random direction by an electron. We will approach this problem by conducting a numerical experiment.

(a) Write a short MATLAB script to calculate the number of 0.1 cm steps a photon will take before it travels a given distance from the center of the Sun. Please include a paragraph explaining the logical steps your code takes to simulate this process. (Note: There are many ways of coding this. I am not asking for a masterpiece, only something that works. It is important to realize that because this is an experiment you will need multiple photons at each distance to gain an understanding of how this works)

(b) Make a ln/ln (the natural log of both values) plot of the average number of steps required for a photon to reach the following distances (1, 2, 3, 4, 5, 10, and 20 cm). Start with $\sim$10 photons for each distance. Do you observe a functional relationship between the number of steps and the distance traveled? Use MATLAB (e.g., the function `polyfit`) to fit the parameters of the function. What is it? Can you explain where this relationship comes from?

(c) Using the functional relationship you found with the aid of the numerical experiment, estimate the average time it will take a photon generated in the center of the sun to reach the Sun's surface.