

## 12.009/18.352 Problem Set 3

Due Thursday, 6 March 2013

Problem 1: 40 pts — (a,b,c,d,e)=(5,10,10,5,10)

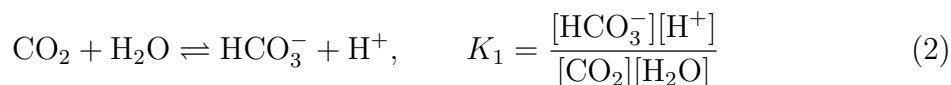
Problem 2: 30 pts — (a,b,c,d)=(10,10,5,5)

Problem 3: 30 pts — (a,b,c)=(15,10,5)

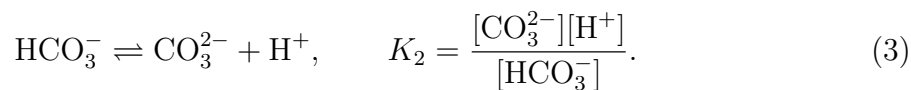
1. *Equilibrium of CO<sub>2</sub> with the Oceans & Timescale of CO<sub>2</sub> Uptake:* In class we discussed how carbon dioxide (CO<sub>2</sub>) leaves a volcano and ends up both in the atmosphere and in the ocean. If CO<sub>2</sub> was not reactive in water then we could predict the concentration of CO<sub>2</sub> 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:

$$[\text{CO}_2] = k_H p_{\text{CO}_2}. \quad (1)$$

Here, [CO<sub>2</sub>] is the concentration of carbon dioxide in the solution (units: M),  $k_H$  is the Henry's law coefficient (a function of the chemical, solvent and temperature, units: M atm<sup>-1</sup>) and  $p_{\text{CO}_2}$  is the partial pressure of carbon dioxide in the gas phase (units: atm; 1 atm=101325 Pa). This works quite well for finding the amount of dissolved gas in a solution. Unfortunately for the purposes of this pset (though fortunately for the habitability of Earth), 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:



and



In the following, we will assume the oceans have a known pH, where you should recall that:

$$\text{pH} = -\log_{10}[\text{H}^+] \quad (4)$$

Because carbon dioxide takes part in these reversible reactions the concentration of carbon dioxide stored in the ocean is not [CO<sub>2</sub>], but rather:

$$[\text{DIC}] = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}], \quad (5)$$

where [DIC] signifies "dissolved inorganic carbon," (units: M).

- (a) Show that the expression for [DIC] as a function of the carbon dioxide concentration, the various equilibrium constants and the hydrogen ion concentration [H<sup>+</sup>]

(i.e. pH), is given by:

$$\begin{aligned} [\text{DIC}] &= k_H^* p_{\text{CO}_2} \\ k_H^* &\equiv k_H \left( 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2} \right) \end{aligned} \quad (6)$$

- (b) Now we will use equation (6) to estimate the partitioning of carbon between the atmosphere and ocean. Assume that the atmosphere has mass  $M_A$  (units: kg), mean molecular weight  $\bar{m}$  (units: kg/mol), a surface pressure of 1 atm, and that  $\text{CO}_2$  is a trace species (has minimal impact on overall atmospheric mass, pressure, etc.). Also assume that the ocean has volume  $V_O$  (units: L). Now, derive an expression for the mass fractions of carbon in the atmosphere and ocean – i.e. how much carbon of a total amount  $C_T$  is found in the ocean as [DIC], and how much is found in the atmosphere as gaseous  $\text{CO}_2$ ? Explain qualitatively how the ocean pH affects these mass fractions.
- (c) At 275 K (i.e. close to the temperature of most of the world’s ocean water)  $k_H = 6.7 \times 10^{-2} \text{ M atm}^{-1}$ ,  $K_1 = 3.3 \times 10^{-7} \text{ M}$ , and  $K_2 = 2.9 \times 10^{-11} \text{ M}$  ( $k_H$ ,  $K_1$ , and  $K_2$  are all fairly temperature-dependent). Look up the mass of Earth’s atmosphere, the volume of the ocean, and the average ocean pH, and estimate the partitioning of carbon between the atmosphere and ocean. For a surface partial pressure  $p_{\text{CO}_2} = 280 \mu\text{-atm}$ , what is the mass of carbon in the atmosphere and ocean?
- (d) The molecular diffusivity  $D_m$  of all of the components of [DIC] in water is on the order of  $10^{-9} \text{ m}^2 \text{ s}^{-1}$ . Using this, and a characteristic ocean depth, derive a time scale for molecular diffusion of carbon from the atmosphere to the bottom of the ocean.
- (e) You should have found a timescale estimate that is quite a bit too large. This is for several reasons, most notably the fact that the ocean is a highly turbulent fluid, allowing for water masses that were originally far from one another to be put in close proximity, and greatly enhancing the surface area over which molecular diffusivity can act. Typical estimates of the ocean’s vertical “eddy diffusivity,” ( $D_{e,v}$ ) or effective diffusivity for a highly turbulent fluid, are  $D_{e,v} \sim 5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ . Thus, diffusion is accelerated by many orders of magnitude due to the interaction of turbulent mixing and molecular diffusion. Consider the surface ocean layer of depth  $H$  which contains as much carbon as the entire atmosphere. What is the timescale for eddy diffusion to this depth and how does it relate to what we have discussed in class? What is the timescale for equilibration of the ocean [DIC] following the addition of a pulse of  $\text{CO}_2$  to the atmosphere? Roughly how much of the  $\text{CO}_2$  in a pulse would stay in the atmosphere for on very long timescales?
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 web-

site. 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  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$ .

- (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*: MATLAB Problem

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 ( $7 \times 10^8$  meters) by the speed of light ( $3 \times 10^8$  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 log-log 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., `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.

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