

## 1.76 Aquatic Chemistry 2005- Problem Set #1

Out: Tuesday, Sept 13<sup>th</sup>

**Due: Tuesday, Sept 27<sup>th</sup>**

Covers Chapter 1 and 2 through p. 70

(Show your work)

Important concepts: Mass balance and electroneutrality equations, the tableau method: choosing correct (independent) components, choosing *good* components, making the correct simplifying assumptions and verifying them, using gaseous phases with tableaux. Log C vs. pH diagrams. Solving equilibrium problems graphically and by approximation. Useful constants are in Table 4.2 (p.161) of the text. Use the “ideal” constants (I=0).

1. Do book problems 1.2 a,f,g, and i. Write out the species and component parts of the tableaux if acceptable.

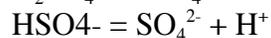
2. River water acquires most of its major ions via the dissolution of minerals in the presence of carbonic acid (from atmospheric CO<sub>2</sub>). To make up a simplified recipe for a river water, I might start with pure water and add the minerals halite (NaCl), gypsum (CaSO<sub>4</sub>·nH<sub>2</sub>O), calcite (CaCO<sub>3</sub>), and magnesite (MgCO<sub>3</sub>), plus a known amount of CO<sub>2</sub>. Suppose I wait long enough so that minerals and the gas dissolve completely. The carbonate minerals and CO<sub>2</sub> together contribute to the “dissolved inorganic carbon” or, simply, total carbon (“C<sub>T</sub>”), present in the water (C<sub>T</sub> = [H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>] + [HCO<sub>3</sub><sup>-</sup>] + [CO<sub>3</sub><sup>2-</sup>]). These species are primarily responsible for the buffering (regulation of pH) of natural waters.

Recipe:            [NaCl]<sub>T</sub> = 1 x 10<sup>-4</sup> M            [MgCO<sub>3</sub>]<sub>T</sub> = 1 x 10<sup>-3</sup> M  
                         [CaSO<sub>4</sub>]<sub>T</sub> = 3 x 10<sup>-4</sup> M            [CO<sub>2</sub>]<sub>T</sub> = 3 x 10<sup>-3</sup> M  
                         [CaCO<sub>3</sub>]<sub>T</sub> = 2 x 10<sup>-3</sup> M

a) 11 species are present at equilibrium.

You only need to consider 3 reactions. What are they?

Why don't we consider these reactions?



Choose the “principal” (i.e. best) set of components (hint: HCO<sub>3</sub><sup>-</sup> should be a component) and set up the equations describing the equilibrium composition of the system defined by the recipe above.

**b)** To gain further practice dealing with tableaux, set up the corresponding equations with the following alternative set of components:  $H^+$ ,  $H_2O$ ,  $NaCl$ ,  $CaSO_4$ ,  $CaCO_3$ ,  $MgCO_3$ ,  $CO_2$ , and  $HCl$ . With this tableau, using only neutral components and  $H^+$ , your TOH equation should look like an electroneutrality expression. Verify that the sets of equations from your two tableaux are equivalent (i.e. that equations from the one set can be added or subtracted to make equations from the other).

**c)** Write a recipe for a solution of identical composition using only the strong acids  $H_2SO_4$  and  $HCl$ , and strong bases  $Ca(OH)_2$ ,  $Mg(OH)_2$ , and  $NaOH$ , and the gas  $CO_2$ .

**d)** Repeat parts a and c with the same recipe except for  $[CO_2]_T = 5 \times 10^{-3} M$ .

**e)** In a bog sediment's interstitial waters, hydrogen sulfide levels may build up as the result of the activity of anaerobic sulfate-reducing bacteria. At the same time, carbon dioxide levels also build up as a result of bacterial respiration. To simulate this situation, I take my river water (from part a.) and bubble it with a gas mixture containing  $CO_2$  and  $H_2S$ :

Same recipe:  $[NaCl]_T = 1 \times 10^{-4} M$        $[MgCO_3]_T = 1 \times 10^{-3} M$   
 $[CaSO_4]_T = 3 \times 10^{-4} M$        $[CO_2]_T = 3 \times 10^{-3} M$   
 $[CaCO_3]_T = 2 \times 10^{-3} M$

plus:  $pCO_2 = 10^{-1.5} atm$   
 $pH_2S = 0.5 atm$

Again, choose the principle components and set up the equilibrium problem defined by this recipe.

Note:  $[CO_2]_T$  is irrelevant in this recipe. Why?

**3.** Determine the equilibrium pH for each of the equilibrium problems you set up in problem # 2 with the help of your tableau and log C vs. pH diagrams (if you are not confident of how to do this, you may first want to do a few of the Practice Problems I handed out). Draw fairly careful diagrams for parts a. and e.- i.e. try to get the slopes and positions of the various lines right; you do not need a new diagram for part d- just indicate how it looks different from part a.  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $SO_4^{2-}$ , and  $Cl^-$  do not need to appear on your diagrams. Why not?

**4. log C. vs. pH diagram- open system:** consider a solution you know to be in equilibrium with 0.5 atm  $H_2S(g)$ . Henry's Law tells us that in this case,

$$\frac{[H_2S](aq)}{pH_2S} = K_{H,H_2S} = 10^{-0.99} Matm^{-1}$$

**a)** What is  $[H_2S]$  if the pH of the solution is 5? 7? 9? (All you know about this solution is that it is in equilibrium with 0.5 atm  $H_2S(g)$ —it could have some other acids or bases in it as well, so the pH could be anything).

Plot  $\log [H_2S]$  vs. pH.

The first  $pK_a$  of  $H_2S$  is 7.0, so  $\frac{[H^+][HS^-]}{[H_2S]} = 10^{-7.0} M$  (note: usually units are not shown).

What is  $[HS^-]$  in this solution if the pH is 5? 7? 9?

The second  $pK_a$  is 13.9. What is  $[S^{2-}]$  if the pH is 5? 7? 9?

Plot both  $\log [HS^-]$  and  $\log [S^{2-}]$  vs. pH on the diagram you started.

Complete the diagram by plotting  $\log [H^+]$  and  $\log [OH^-]$  vs. pH.

The information on this diagram will be valid for any solution in equilibrium with 0.5 atm  $H_2S(g)$ .

**b)** Suppose you made a solution by letting pure water equilibrate with 0.5 atm  $H_2S(g)$ . Make two tableaux for this system, one with  $HS^-$  as a component and the other with  $H_2S$  as the component. Why is it better to choose  $H_2S$  as a component? What is the TOTh equation in this case? Identify the only place on your diagram where this equation is satisfied. Calculate the pH of the solution.

**c)** Calculate the pH for a solution containing 0.005 M sodium hydroxide, completely dissolved and in equilibrium with 0.5 atm  $H_2S(g)$ . (Hint: will the pH be higher or lower than your answer from part b?)

**d)** Calculate the pH of a solution containing 0.001 M  $[HNO_3]_T$  in equilibrium with 0.5 atm  $H_2S(g)$ .

**5.** Discuss what is meant by “open” and “closed” systems in the context of aquatic chemistry equilibrium calculations. Suppose you are asked to construct an equilibrium model for the acid-base chemistry of a lake. What questions would you ask to help decide whether to model the lake as “open” or “closed” with respect to both gaseous and solid phases?