## 1.76 Aquatic Chemistry 2005- Problem Set #2

Out: Tuesday, Sept 27th
**Due: Thursday, Oct 13th**

Covers Chapter 1 and 2

Important concepts: more practice solving equilibrium problems; $\Delta G$, free energies and equilibrium constants; temperature, pressure, and ionic strength effects on equilibrium.

**In all problems: neglect ionic strength effects unless told otherwise. Show your work...**

**1.** The idea of these problems is to give you more practice and intuition with equilibrium problems (especially in carbonate buffer systems). Find the equilibrium composition of each of the following systems (you can sketch log C-pH diagrams if you find this helpful.) When you have solved the problem, give a 2-3 sentence "intuitive" chemical explanation describing what took place.

*Example:*
For the recipe $[HCl]_T = 10^{-3}$ M, $[NaHCO_3]_T = 5x10^{-4}$ M,
your equilibrium composition will be:

| | | |
|---|---|---|
| $[Na^+] = 5x10^{-4}$ M | $[Cl^-] = 10^{-3}$ M | $[H^+] = 5x10^{-4}$ M |
| $[H_2CO_3^*] = 5x10^{-4}$ M | $[HCO_3^-] = 5x10^{-7}$ M | $[CO_3^{2-}] = 5x10^{-14}$ M |
| $[OH^-] = 2x10^{-11}$ M | | |

Your "explanation" could sound like this:

*The HCl and $NaHCO_3$ dissociated completely. Just about all of the $HCO_3^-$ then reacted with $H^+$ to make $H_2CO_3^*$. The equilibrium $[H^+]$ is given by the excess of the strong acid HCl over the weak base $NaHCO_3$.*

a.) $[HCl]_T = 3x10^{-4}$ M, $[NaOH]_T = 5x10^{-4}$ M

b.) $[NaHCO_3]_T = 10^{-3}$ M, $[HCl]_T = 2x10^{-4}$ M

c.) $[CO_2]_T = 10^{-2}$ M, $[NaOH]_T = 2x10^{-3}$ M

d.) $pCO_2 = 10^{-2.5}$ atm, $[NaOH]_T = 10^{-3}$ M

**2.** The dissolution and precipitation of the mineral calcite ($CaCO_{3(s)}$) has important effects on the composition of natural waters. The chemical potential of the pure solid calcite ($CaCO_{3(s)}$)is given by:

$$\mu_{CaCO3} = \mu^{o}_{CaCO3}$$

a.) Use this expression to show that the equilibrium expression of the reaction

$$CaCO_{3(s)} = Ca^{2+} + CO_3^{2-}$$

takes the form $\{Ca^{2+}\}\{CO_3^{2-}\} = K_{sp}$

b.) Use the attached thermodynamic data to calculate the value of $K_{sp}$ at standard temparature and pressure (note: $G^{o}_{f}$ means the same thing as $\mu^{o}$).

c.) Use the attached data to estimate the value of $K_{sp}$ at 4°C. Compare your calculated answer to the data shown in Figure 2.5 (p. 88) of the Morel and Hering textbook. What assumption was inherent in your calculation, and (comparing Figure2.5) does it seem like a good assumption to you?

d.) Calculate an "apparent" solubility product of calcite, $K_{sp,app} = [Ca^{2+}][CO_3^{2-}]$, for standard temperature and pressure at ionic strengths of 0.0004 and 0.2 M.

e.) Suppose you are modeling the solubility of calcite in a lake whose temperature can vary over the year between 4°C and 25°C and whose ionic strength is about 0.0004 M. If your uncertainty in the relevant equilibrium constants, measured pH of the lake, etc. is about ±0.05 log units, is it important to worry about both temperature and ionic strength effects (i.e. is the error introduced by temperature and pH effects greater than the uncertainty in the values of these constants)? Or can you get away with neglecting either temperature or ionic strength corrections (or both)?

3. Book problem 2.3, parts a, b and c **only**

parts a) and b) use the **molar scale only**.

part b) remember that $\Delta G = \delta G/\delta\xi$

Feel free to use a computer to do the calculation and draw the graph, but you must show us the equations you gave the computer.

4. Do book problem 2.8.

**5. Mindstretcher – Spaceship Earth**

*(Note: "Mindstretcher" problems are meant to encourage you to think about what you are learning in more open-ended contexts. It is quite possible to write term papers on the questions posed below -- DON'T. Just try to come up with a few good thoughts on each of the questions, and explain them clearly...)*

Think of the biosphere of Planet Earth as a thermodynamic system: energy enters the system in the form of sunlight, and leaves as blackbody radiation, but there is (approximately) no transfer of matter across the boundaries of this system.

Give some examples of the first and second laws of thermodynamics as they relate to the earth's biosphere, e.g. examples of energy being converted from one form to another, capacity to work being lost as heat etc. Discuss what happens to energy and entropy in the different trophic levels of an ecosystem (primary producers, herbivores, carnivores, decomposers). Note that production of biomass and $O_2$ from $CO_2$, nutrients, and water is a highly endergonic process ($\Delta G >> 0$). Would life on earth be possible without sunlight?

**Table 3A. (*Continued*)**  FROM Stumm Morgan Aquatic Chemistry 3' Edition

| Species | Formation from the Elements $\overline{G}_f^0$ (kJ $mol^{-1}$) | Formation from the Elements $\overline{H}_f^0$ (kJ $mol^{-1}$) | Entropy $\overline{S}^0$ (J $mol^{-1}$ $K^{-1}$) | Reference[c] |
|---|---|---|---|---|
| Br (Bromide) | | | | |
| $Br_2$(l) | 0 | 0 | 152 | NBS |
| $Br_2$(aq) | 3.93 | −259 | 130.5 | NBS |
| $Br^-$(aq) | −104.0 | −121.5 | 82.4 | NBS |
| HBrO(aq) | −82.2 | −113.0 | 147 | NBS |
| $BrO^-$(aq) | −33.5 | −94.1 | 42 | NBS |
| C (Carbon) | | | | |
| C (Graphite) | 0 | 0 | 152 | NBS |
| C (Diamond) | 3.93 | −2.59 | 130.5 | NBS |
| $CO_2$(g) | −394.37 | −393.5 | 213.6 | NBS |
| $H_2CO_3^*$(aq) | −623.2 | −699.6 | 187.0 | R[d] |
| $H_2CO_3$(aq) ("true") | ~ −607.1 | | | S |
| $HCO_3^-$(aq) | −586.8 | −692.0 | 91.2 | S |
| $CO_3^{2-}$(aq) | −527.9 | −677.1 | −56.9 | NBS |
| $CH_4$(g) | −50.79 | −74.80 | 186 | NBS |
| $CH_4$(aq) | −34.39 | −89.04 | 83.7 | NBS |
| $CH_3OH$(aq) | −175.4 | −245.9 | 133 | NBS |
| HCOOH(aq) | −372.3 | −425.4 | 163 | NBS |
| $HCOO^-$(aq) | −351.0 | −425.6 | 92 | NBS |
| $CH_2O$(aq) | −129.7 | | | |
| $CH_2O$(g) | −110.0 | −116.0 | 218.6 | S |
| HCN(aq) | 112.0 | 105.0 | 129 | NBS |
| $CN^-$(aq) | 166.0 | 151.0 | 118 | NBS |
| COS(g) | −169.2 | −137.2 | 234.5 | NBS |
| $CNS^-$(aq) | 88.7 | 72.0 | | S |
| $H_2C_2O_4$(aq) | −697.0 | −818.26 | | S |
| $HC_2O_4^-$(aq) | −690.86 | −818.8 | | S |
| $C_2O_4^{2-}$(aq) | −674.04 | −818.8 | 45.6 | S |
| Ca (Calcium) | | | | |
| $Ca^{2+}$(aq) | −553.54 | −542.83 | −53 | R |
| $CaOH^+$(aq) | −718.4 | | | NBS |
| $Ca(OH)_2$(aq) | −868.1 | −1003 | −74.5 | NBS |
| $Ca(OH)_2$ (Portlandite) | −898.4 | −986.0 | 83 | R |
| $CaCO_3$ (Calcite) | −1128.8 | −1207.4 | 91.7 | R |
| $CaCO_3$ (Aragonite) | −1127.8 | −1207.4 | 88.0 | R |
| $CaMg(CO_3)_2$ (Dolomite) | −2161.7 | −2324.5 | 155.2 | R |
| $CaSiO_3$ (Wollastonite) | −1549.9 | −1635.2 | 82.0 | R |
| $CaSO_4$ (Anhydrite) | −1321.7 | −1434.1 | 106.7 | R |
| $CaSO_4 \cdot 2\,H_2O$ (Gypsum) | −1797.2 | −2022.6 | 194.1 | R |
| $Ca_5(PO_4)_3OH$ (Hydroxyapatite) | −6338.4 | −6721.6 | 390.4 | R |
| Cd (Cadmium) | | | | |
| Cd (γ-Metal) | | | | |
| $Cd^{2+}$(aq) | −77.58 | −75.90 | −73.2 | R |
| $CdOH^+$(aq) | −284.5 | | | R |
| $Cd(OH)_3^-$(aq) | −600.8 | | | R |
| $Cd(OH)_4^{2-}$(aq) | −758.5 | | | R |
| $Cd(OH)_2$(aq) | −392.2 | | | R |
| CdO (s) | −228.4 | −258.1 | 54.8 | |
| $Cd(OH)_2$ (precip.) | −473.6 | −560.6 | 96.2 | R |
| $CdCl^+$(aq) | −224.4 | −240.6 | 43.5 | R |
| $CdCl_2$(aq) | −340.1 | −410.2 | 39.8 | R |