

**Homework #6**

1. Determine the pH and alkalinity for the following solutions. Assume the systems are closed to the atmosphere.
- $5 \times 10^{-4} \text{F NaOH}$
  - $5 \times 10^{-5} \text{F Na}_2\text{CO}_3$
  - $5 \times 10^{-5} \text{F KHCO}_3$
  - $1 \times 10^{-3} \text{F HCl}$

**Solution to #1**

Please note that alkalinity in these problems can be most easily determined by the sum of the base cations minus the acid anions ( $\text{Alk} = C_B - C_A$ ).

a.  $5 \times 10^{-4} \text{F NaOH}$

This is a strong base,

$$[\text{OH}^-] = [\text{Na}^+] = 5 \times 10^{-4}$$

$\text{pH} = 10.7$
$\text{Alk} = 5 \times 10^{-4} \text{ eq/L} = 25 \text{ mg/L as CaCO}_3$

b.  $5 \times 10^{-5} \text{F Na}_2\text{CO}_3$

This is a weak base. The problem can be solved with a log C vs pH diagram and the following proton balance equation:

$$2[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{H}^+] = [\text{OH}^-]$$

which reduces to:

$$[\text{HCO}_3^-] = [\text{OH}^-]$$

$\text{pH} = 9.7$
$\text{Alk} = 10^{-4} \text{ eq/L} = 5 \text{ mg/L as CaCO}_3$

c.  $5 \times 10^{-5} \text{F KHCO}_3$

This is a weak base. The problem can be solved with a log C vs pH diagram and the following proton balance equation:

$$[\text{H}_2\text{CO}_3] + [\text{H}^+] = [\text{OH}^-] + [\text{CO}_3^{2-}]$$

which reduces to:

$$[\text{H}_2\text{CO}_3] = [\text{OH}^-]$$

pH = 8.0
Alk = $5 \times 10^{-5}$ eq/L = 2.5 mg/L as CaCO <sub>3</sub>

d.  $1 \times 10^{-3}$ F HCl

This is a strong acid,

$$[Cl^-] = [H^+] = 1 \times 10^{-3}$$

pH = 3
Alk = $-1 \times 10^{-3}$ eq/L = -50 mg/L as CaCO <sub>3</sub>

2. What partial pressure of carbon dioxide are the solutions from question #1 in equilibrium with?

Please note that while closed systems may not have any open air/water interface, there is still a calculated value for the partial pressure of CO<sub>2</sub> that the solution is in equilibrium with, and that value is often non-zero. Also note that many closed systems do have air/water interfaces, but they may be considered closed because either (1) the interface has not existed long enough to allow for equilibrium to have occurred, or (2) the volume of the air space is too small to affect the CO<sub>2</sub> concentration in the water.

$$[H_2CO_3^*] = k_H p_{CO_2}$$

$$[H_2CO_3^*] = \alpha_0 C_T$$

$$p_{CO_2} = \frac{C_T \alpha_0}{k_H}$$

Since:

$$Alk = \alpha_1 C_T + 2\alpha_2 C_T + [OH^-] - [H^+]$$

Then:

$$C_T = \frac{Alk - [OH^-] + [H^+]}{\alpha_1 + \alpha_2}$$

And:

$$p_{CO_2} = \frac{(Alk - [OH^-] + [H^+])\alpha_0}{(\alpha_1 + \alpha_2)k_H}$$

In most cases it reduces to:

$$p_{CO_2} = \frac{(Alk)\alpha_0}{(\alpha_1 + \alpha_2)k_H}$$

a.  $5 \times 10^{-4}$ F NaOH

$C_T = 0$ , so:

$$p_{\text{CO}_2} = 0$$

b.  $5 \times 10^{-5} \text{F Na}_2\text{CO}_3$

$C_T = 5 \times 10^{-5}$ , and  $\text{pH} = 9.7$ , so:  
 $\alpha_0 \sim [\text{H}^+]/k_1 = 10^{-9.7}/10^{-6.3} = 10^{-3.4}$   
 $p_{\text{CO}_2} = 5 \times 10^{-5} (10^{-3.4})/10^{-1.5}$

$$p_{\text{CO}_2} = 6.3 \times 10^{-7} = 10^{-6.2}$$

You can also do this by using the  $[\text{H}_2\text{CO}_3^*]$  determined for problem 1b, but note that this value is really  $[\text{H}_2\text{CO}_3^*]$  which is about equal to the aqueous carbon dioxide concentration  $[\text{CO}_2(\text{aq})]$ . Therefore, there is no need to multiply by 630 (i.e., the ratio of  $[\text{CO}_2(\text{aq})]/[\text{H}_2\text{CO}_3^*]$ ).

c.  $5 \times 10^{-5} \text{F KHCO}_3$

$C_T = 5 \times 10^{-5}$ , and  $\text{pH} = 8.0$ , so:  
 $\alpha_0 \sim [\text{H}^+]/k_1 = 10^{-8.0}/10^{-6.3} = 10^{-1.7}$   
 $p_{\text{CO}_2} = 5 \times 10^{-5} (10^{-1.7})/10^{-1.5}$

$$p_{\text{CO}_2} = 3.2 \times 10^{-5} = 10^{-4.5}$$

d.  $1 \times 10^{-3} \text{F HCl}$

$C_T = 0$ , so:

$$p_{\text{CO}_2} = 0$$

3. Repeat question #1, but assume the systems are open to the atmosphere.

### Solution to #3 (1 point)

Draw an open system, log C vs pH diagram, and solve using the electroneutrality equation.

a.  $5 \times 10^{-4} \text{F NaOH}$

ENE:

$$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

which reduces to:

$$[\text{Na}^+] = [\text{HCO}_3^-]$$

$$\text{pH} = 8.0$$

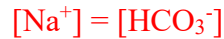
$$\text{Alk} = 5 \times 10^{-4} \text{ eq/L} = 25 \text{ mg/L as CaCO}_3$$

b.  $5 \times 10^{-5} \text{F Na}_2\text{CO}_3$

ENE:



which reduces to:



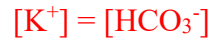
pH = 7.3
Alk = $1 \times 10^{-4}$ eq/L = 5 mg/L as CaCO <sub>3</sub>

c.  $5 \times 10^{-5}$ F KHCO<sub>3</sub>

ENE:



which reduces to:



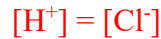
pH = 7.0
Alk = $5 \times 10^{-5}$ eq/L = 2.5 mg/L as CaCO <sub>3</sub>

d.  $1 \times 10^{-3}$ F HCl

ENE:



which reduces to:



pH = 3
Alk = $-1 \times 10^{-3}$ eq/L = -50 mg/L as CaCO <sub>3</sub>

4. A groundwater was found to have the following composition:

$$\text{ANC} = 3 \times 10^{-2} \text{ eq/L}, \quad \text{pH} = 7.5$$

What is the partial pressure of CO<sub>2</sub> that is in equilibrium with this water?

### Solution to #4

Assume all ANC is due to carbonate species; which at pH 7.5 is almost entirely bicarbonate.  
Therefore:

$$[\text{HCO}_3^-] = 3 \times 10^{-2}$$

and since

$$[\text{H}_2\text{CO}_3^*] = [\text{HCO}_3^-][\text{H}^+]/k_1$$

so:

$$[\text{H}_2\text{CO}_3^*] = (3 \times 10^{-2})(10^{-7.5})/10^{-6.3}$$

$$[\text{H}_2\text{CO}_3^*] = 10^{-2.7}$$

now:

$$[\text{H}_2\text{CO}_3^*] = k_H \times p_{\text{CO}_2}$$

$$p_{\text{CO}_2} = 10^{-2.7}/10^{-1.5} = 10^{-1.2} = 0.063 \text{ atm}$$

5. A surface water and a groundwater are to be used as a raw water supply for the town of Springfield, FL. They will be mixed as follows:

	<u>Surface Water</u>	<u>Groundwater</u>
Flow Rate	3.5 MGD	0.8 MGD
Alkalinity	10 mg/L as CaCO <sub>3</sub>	250 mg/L as CaCO <sub>3</sub>
pH	6.9	8.3

What will the pH of the combined waters be?

### Solution to #5

Recognize that this must be a closed system. The mixing of waters within an engineered treatment system that does not specifically include aeration or multi-day open-air storage will not result in substantial transfer of CO<sub>2</sub> across the air water interface.

Also recognize that a high level of precision (i.e., significant figures) is needed for the intermediate calculations in order to have an accurate value for the difference between the total carbonates (C<sub>T</sub>) and the alkalinity (Alk). This is key to getting an accurate value for the blended pH.

The final pH should be somewhere between the pHs of the two waters being blended. If you get a pH outside of this range, you should be suspicious that a mistake was made. You can also use a nomograph to check very roughly on your result. However, don't rely on nomographs for accurate determination of blended water pH. They usually cannot be read with an adequate degree of accuracy.

First Calculate C<sub>T</sub> for both waters:

$$C_T = \frac{\text{Alk} - [\text{OH}^-] + [\text{H}^+]}{\alpha_1 + 2\alpha_2}$$

$$\text{Surface Water: } C_T = ((10/50,000) - 10^{-7.1} + 10^{-6.9})/0.78048 = 2.563 \times 10^{-4} \text{ M} = 10^{-3.59}$$

$$\text{Groundwater: } C_T = ((250/50,000) - 10^{-5.7} + 10^{-8.3})/0.99815 = 5.007 \times 10^{-3} \text{ M} = 10^{-2.30}$$

Next Determine the Blended C<sub>T</sub> and Alk

$$C_{T(\text{blend})} = (3.5(2.563 \times 10^{-4}) + 0.8(5.007 \times 10^{-3}))/ (3.5 + 0.8) = 1.140 \times 10^{-3} \text{ M}$$

$$\text{Alk}_{(\text{blend})} = (3.5(10/50,000) + 0.8(250/50,000))/ (3.5 + 0.8) = 1.093 \times 10^{-3} \text{ eq/L}$$

Lastly, Determine pH of the Blended Water

Since the pH of both waters is well below the pk<sub>2</sub>, carbonate is likely to be insignificant as compared to bicarbonate. This means that the alkalinity is composed almost entirely of bicarbonate, so:

$$\begin{aligned}
 Alk &\cong \alpha_1 C_T \\
 &\cong \left( \frac{1}{\frac{[H^+]}{k_1} + 1 + \frac{k_2}{[H^+]}} \right) C_T \\
 &\cong \frac{C_T}{\frac{[H^+]}{k_1} + 1}
 \end{aligned}$$

now insert Alk and  $C_T$  and solve for  $H^+$ , and we get:

$$[H^+] = 1.87 \times 10^{-8}$$

6. You are treating an alkaline groundwater by alum coagulation followed by base addition for corrosion control. Your target pH for the water in the distribution system is 8.5. Analysis of the finished water prior to base addition shows a pH of 7.2, and an alkalinity of 250 mg/L as  $CaCO_3$ . How much of either one of the following two bases would you have to add (in mg/L) to reach your target pH.
- Caustic Soda ( $NaOH$ )
  - Soda Ash ( $Na_2CO_3$ )

Solution to #6

This is a closed system. Recall that:

$$\begin{aligned}
 Alk &= (\alpha_1 + 2\alpha_2)C_T + [OH^-] - [H^+] \\
 &\cong (\alpha_1 + 2\alpha_2)C_T
 \end{aligned}$$

We also know that:

$$Alk = 250 \text{ mg/L as } CaCO_3 = 5 \times 10^{-3} \text{ equivalents/L}$$

a. Caustic Soda

Since caustic soda does not contain carbonates,  $C_T$  is a constant for this case.

@ pH 7.2,

$$\begin{aligned}
 C_T &= \frac{Alk}{\alpha_1 + 2\alpha_2} \\
 &= \frac{5 \times 10^{-3}}{0.8876 + 0.00141} \\
 &= 5.6245 \times 10^{-3} \text{ M}
 \end{aligned}$$

Next, it's a simple matter of calculating the change in alkalinity that accompanies the change in pH.

$$Alk = (\alpha_1 + 2\alpha_2)C_T$$

@ pH 8.5,

$$\begin{aligned}\text{Alk} &= (0.97832 + 2 * 0.015505) * 5.6245 \times 10^{-3} \\ \text{Alk} &= 5.67699 \times 10^{-3} \text{ equivalents/L}\end{aligned}$$

$$\begin{aligned}\text{delta Alkalinity} &= 5.67699 \times 10^{-3} \text{ equivalents/L} - 5 \times 10^{-3} \\ &= 6.77 \times 10^{-4} \text{ equivalents}\end{aligned}$$

and this change in alkalinity must come from the caustic soda added:

$$\text{Caustic Soda Dose} = 6.77 \times 10^{-4} \text{ equ.} * 40 \text{g/equ.}$$

$$\text{Caustic Soda Dose} = 27.1 \text{ mg/L}$$

b. Soda Ash

This problem is similar to part "a", except that  $C_T$  is augmented by addition of the soda ash. It can be directly related to the soda ash dose (SAD), knowing that one mole of soda ash contains one mole of carbonate species:

$$C_{T\text{-final}} = C_{T\text{-initial}} + \text{SAD}$$

We can then use this and estimate final Alkalinity ( $\text{Alk}_{\text{final}}$ ) as a function of SAD using the two different equations for alkalinity, then solve both for SAD. (N.B. you can also solve this problem by recognizing that addition of soda ash does not change the acidity. You then use this acidity to solve for final carbonate concentration which then gives you the SAD).

*First equation*

$$\begin{aligned}\text{Alk}_{\text{final}} &= (C_B - C_A)_{\text{final}} \\ &= \text{Alk}_{\text{initial}} + 2 * \text{SAD} \\ &= 5 \times 10^{-3} + 2 * \text{SAD}\end{aligned}$$

*Second Equation*

$$\begin{aligned}\text{Alk}_{\text{final}} &\cong (\alpha_1 + 2\alpha_2)_{\text{final}} * C_{T\text{-final}} \\ &\cong (0.97832 + 2 * 0.015505) * (5.6245 \times 10^{-3} + \text{SAD}) \\ &\cong 5.67699 \times 10^{-3} + 1.00933 * \text{SAD}\end{aligned}$$

*Combine and Solve*

$$\begin{aligned}5 \times 10^{-3} + 2 * \text{SAD} &= 5.67699 \times 10^{-3} + 1.00933 * \text{SAD} \\ \text{SAD} &= 6.83 \times 10^{-4} \text{ M}\end{aligned}$$

*Convert to mg/L soda ash*

$$\begin{aligned}\text{Soda Ash Dose} &= (6.83 \times 10^{-4} \text{ moles/L}) * (106 \text{ g/mole}) \\ &= 0.0724 \text{ g/L} \\ &= 72 \text{ mg/L}\end{aligned}$$

*Assigned: 25 Mar 20*  
*Due: 1 Apr 20*