Aquatic Chem - 1.76 - 2005
PSET # 3 Solutions

PROBLEM 1: BOOK PROBLEM 4.1

a) $[NaOH]_T = 10^{-3}\ M$

$[NaHCO_3]_T = 10^{-2}\ M$

$pCO_2 = 10^{-2.5}$ atm

"Recipe part of Alk Tableau"

	H_2O	H^+	$H_2CO_3^*$	Na^+
$[NaOH]_T$	1	-1		1
$[NaHCO_3]_T$		-1	1	1
$[CO_2]_T$	-1		1	

$$Alk = -TOTH = [NaOH]_T + [NaHCO_3]_T$$

$$= 10^{-3}\ M + 10^{-2}\ M = 1.\underline{1} \times 10^{-2}\ M = \boxed{1 \times 10^{-2}\ M}$$

b) $[Na_2CO_3]_T = 10^{-4} M$

$[NH_3]_T = 10^{-2} M$

$pCO_2 = 10^{-2.5}$ atm

$$(NH_4^+ \underset{9.24}{\rightleftharpoons} NH_3 + H^+)$$

↑ dominates at CO_2 eq. pt ($pH \sim 4$-5), choose as Alk component

	H_2O	H^+	$H_2CO_3^*$	NH_4^+	Na^+
$[Na_2CO_3]_T$		-2	1		2
$[NH_3]_T$		-1		1	
$[CO_2]_T$	-1	0	1		

$$Alk = -TOTH = 2[Na_2CO_3]_T + [NH_3]_T = 2 \times 10^{-4} M + 10^{-2} M$$

$$= 1.0\underline{2} \times 10^{-2}\ M = \boxed{10^{-2}\ M}$$

c) Carbonate system only; $pCO_2 = 10^{-3.5}$ atm; $pH = 7.3$.

$$C\text{-}Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

Rewrite spp. in terms of pH, $H_2CO_3^*$ (fixed by eq. with pCO_2):

$$C\text{-}Alk = \frac{(K_{a1})[H_2CO_3^*]}{[H^+]} + \frac{(2)(K_{a2})[HCO_3^-]}{[H^+]} + \frac{K_W}{[H^+]} - [H^+]$$

$$= \frac{(K_{a1})(K_H)(pCO_2)}{[H^+]} + \frac{2(K_{a2})(K_{a1})(K_H)(pCO_2)}{[H^+]^2} + \frac{K_W}{[H^+]} - [H^+]$$

$$\text{C-Alk} = \frac{(10^{-6.35})(10^{-1.46})(10^{-3.5})}{10^{-7.3}} + \frac{2(10^{-10.33})(10^{-6.35})(10^{-1.46})(10^{-3.5})}{(10^{-7.3})(10^{-7.3})}$$

$$+ \frac{10^{-14}}{10^{-7.3}} + 10^{-7.3}$$

$$= 10^{-4.01} + 2(10^{-7.04}) + 10^{-6.7} + 10^{-7.3}$$

$$\boxed{\text{Alk} = 10^{-4.01}\ M}$$

d) $[H_2SO_4]_T = [NaHCO_3]_T = 10^{-3}\,M$

$H_2SO_4 \rightarrow \underset{pK_a \sim 2}{HSO_4^-} \rightleftharpoons H^+ + \underset{\uparrow}{SO_4^{2-}}$

dominant @pH 4-5.

	H_2O	H^+	$H_2CO_3^*$	SO_4^{2-}	Na^+
$[H_2SO_4]_T$		2		1	
$[NaHCO_3]_T$		-1	1		1

$\text{Alk} = -\text{TOTH} = 1[NaHCO_3]_T - 2[H_2SO_4]_T = 10^{-3}M - 2(10^{-3}M)$

$$\boxed{= -10^{-3}M}$$

Problem 2 : Book Prob 4.4

a) $HS^- + H^+ \rightarrow H_2S(g)$

	H_2O	H^+	H_2S
$[H_2S]_T$		0	1

$H_2S \rightleftharpoons H^+ + HS^-$ $pK_a = 7.02$

$HS^- \rightleftharpoons H^+ + S^{2-}$ $pK_a = 13.9$

dominant at pH ~ 4-5

$\Delta\text{Alk} = -\Delta\text{TOTH} =$ $\boxed{0\ M \Rightarrow \text{escape of } H_2S \text{ has no alkalinity effect.}}$

b) $SO_4^{2-} + 2\text{"}CH_2O\text{"} \rightarrow HS^- + 2HCO_3^- + H^+$; rewrite in Alk components:

$SO_4^{2-} + 2\text{"}CH_2O\text{"} + 2H^+ \rightarrow H_2S + 2H_2CO_3^*$

$\Delta\text{Alk} = (-1)(\Delta[H^+]) = (-1)(-2\times10^{-3}M) =$ $\boxed{2\times10^{-3}M \text{ Alk produced.}}$

c) $NH_4^+ \rightarrow NH_3(g) + H^+$

	H_2O	H^+	NH_4^+
$[NH_3]_T$		-1	1

$$\Delta Alk = -(\Delta TOTH) = 1(\Delta[NH_3])$$
$$= 1(-10^{-3}M)$$
$$\boxed{= -10^{-3}\,M}$$

⇒ alk consumed with $NH_3(g)$ escape.

d) $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2(g) + H_2O$

$Ca^{2+} + 2H_2CO_3^* \rightarrow CaCO_3(s) + CO_2(g) + H_2O + 2H^+$

$$\Delta Alk = -1(\Delta[H^+]) = (-1)(2[+10^{-3}M]) = \boxed{-2\times10^{-3}\,M}$$

PROBLEM 3: BOOK PROBLEM 4.12

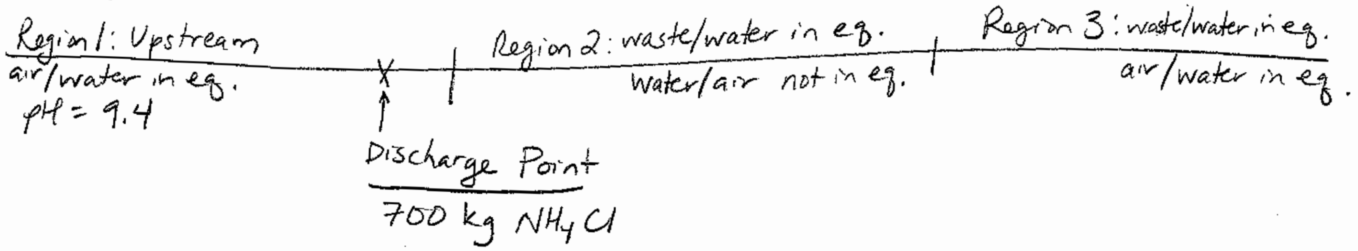
Atm: 0.032% = partial pressure CO_2

0.0000% = partial pressure NH_3 (so now they decide to give us sig figs!)

Assume Total P = 1 atm.

Q = flow rate = 2 m²/s

The very flat river:



a) Assume the carbonate species are the principle buffering species.

Then $Alk = C\text{-}Alk = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$, where

$[OH^-] = K_w/[H^+]$

$[HCO_3^-] = (K_{a_1})[H_2CO_3^*]/[H^+] = (K_{a_1})(K_H)(pCO_2)/[H^+]$

$[CO_3^{2-}] = (K_{a_2})[HCO_3^-]/[H^+] = (K_{a_2})(K_{a_1})(K_H)(pCO_2)/[H^+]^2$

$[H^+] = 10^{-pH} = 10^{-9.4}$

$pCO_2 = (0.00032)(1\,atm) = 3.2\times10^{-4}\,atm = 10^{-3.49}\,atm$

Assuming that Na^+ is the major cation, electroneutrality gives

$$[OH^-] + [HCO_3^-] + 2[CO_3^{2-}] = [H^+] + [Na^+]$$

$$[Na^+] = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] = Alk.$$

$$= -10^{-9.4} + \frac{10^{-14}}{10^{-9.4}} + \left[\frac{(10^{-6.35})(10^{-1.46})(10^{3.49})}{10^{-9.4}}\right]\left(1 + \frac{2(10^{-10.33})}{10^{-9.4}}\right)$$

$$= -10^{-9.4} + 10^{-4.6} + 10^{-1.9} + 2(10^{-2.85}) = \boxed{10^{-1.8}\,M}$$

b) Region 1 has a measured pH of 9.4.

A weak acid, NH_4Cl, is added to the system and equilibrates with the water.

$$NH_4Cl\,(aq) \longrightarrow NH_4^+ + Cl^- \qquad \text{assume complete dissol}^{n}.$$

$$NH_4^+ \rightleftharpoons NH_3\,(aq) + H^+ \qquad pKa = 9.2$$

The carbonate system is likely to buffer the addition of this weak acid, and slight decreases in pH may be observed in Region 2.

After equilibrating with the atmosphere, $NH_3\,(g)$, will have escaped the system, driving $NH_4^+ \rightleftharpoons NH_3\,(aq) + H^+$ completely to the right, decreasing the pH. This will result in this rxn: $H_2CO_3^* \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$ being driven to the left, and $CO_2\,(g)$ will escape the system as it equilibrates with the atmosphere. This will cause an increase in the pH. We will have to solve the problem to see which process dominates, but we can guess that pH, region 3 $\simeq$ pH, region 1 $>$ pH, region 2.

c) spp:
NH_4^+, $NH_3(aq)$, Cl^-, $H_2CO_3^*$, HCO_3^-, CO_3^{2-}, H^+, OH^-, H_2O, Na^+

Mass laws:

$$K_a = 10^{-9.24} = \frac{[H^+][NH_3(aq)]}{[NH_4^+]}$$

$$K_w = 10^{-14} = [OH^-][H^+]$$

10 spp − 4 eqn = 6 components

$$K_{a_1} = 10^{-6.35} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}$$

$$K_{a_2} = 10^{-10.33} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

	H_2O	H^+	HCO_3^-	NH_4^+	Na^+	Cl^-
H_2O	1	0				
OH^-	1	-1				
H^+		1				
$H_2CO_3^*$		1	1			
HCO_3^-			1			
CO_3^{2-}		-1	1			
NH_4^+		0		1		
NH_3		-1		1		
Na^+		0			1	
Cl^-		0				1
$[NH_4Cl]_T$		0		1		1
$[H_2O]_T$	1	0				

TOT NH_4^+: $[NH_4^+] + [NH_3(aq)] = [NH_4Cl]_T$

TOT Na^+: $[Na^+] = 10^{-1.8}$ M, from part a.

TOT Cl^-: $[Cl^-] = [NH_4Cl]_T$

TOT HCO_3^-: $[H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = ?$

TOT HCO_3^-: $[H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = \ ? \ = C_{T,2}$

We have no recipe ingredients! However, we know That $C_{T,1} = C_{T,2}$, as there is no equilibration with the atmosphere (and we cannot access the mineral dissol'n do to lack of info.).

$$C_{T,1} = C_{T,2} = (10^{-1.46})(10^{-3.49}) + 10^{-1.9} + 10^{-2.83}$$
$$= 1.4 \times 10^{-2}\ M = 10^{-1.85} = \boxed{10^{-1.9}\ M = C_{T,2}}$$

TOT H^+: $[H^+] - [OH^-] + [H_2CO_3^*] - [CO_3^{2-}] - [NH_3] = \ ?$

Again, we have no recipe ingredients!
Perhaps Alk can help us...

$$Alk_2 = -[H^+] + [OH^-] + [NH_3(aq)] + [HCO_3^-] + 2[CO_3^{2-}]$$
$$= Alk_1 + \Delta Alk.$$

$\Delta Alk = ?$ Added $[NH_4Cl]_T$; Recipe in Alk Tableau:

	H_2O	H^+	NH_4^+	Cl^-
$[NH_4Cl]_T$		0	1	1

$$\Delta Alk = 0(\Delta[NH_4Cl]_T)$$
$$= 0.$$

Then $Alk_2 = Alk_1 + 0 = 10^{-1.8} M$, as calculated in part a.

$$\boxed{Alk_2 = -[H^+] + [OH^-] + [NH_3(aq)] + [HCO_3^-] + 2[CO_3^{2-}] = 10^{-1.8} M}$$

If we can write these in terms of pH and other known quanities, we can solve for pH!!

$[H^+] = 10^{-pH}$

$[OH^-] = 10^{-14}/10^{-pH}$

$[NH_3(aq)]$:

$$[NH_4Cl]_T = [NH_4^+] + [NH_3]$$

$$= \frac{[H^+][NH_3]}{Ka} + [NH_3] = [NH_3]\left(\frac{10^{-pH}}{10^{-9.24}} + 1\right)$$

$$[NH_3] = [NH_4Cl]_T \Big/ \left(10^{-pH+9.2} + 1\right)$$

$$[NH_4Cl]_T = ?$$

$$\frac{700\,kg}{hr} \times \frac{mol}{53.49\,g} \times \frac{1000\,g}{kg} = 1.3 \times 10^4\,mol/hr$$ NH_4Cl added to stream.

$$\frac{2\,m^3}{s} \times \frac{L}{10^{-3}\,m^3} \times \frac{60\,s}{min} \times \frac{60\,min}{hr} = 7.2 \times 10^6\,L/hr$$ flow rate.

Assuming NH_4Cl has constant rate of addition, discharge is equivalent to

$$\frac{1.3 \times 10^4\,mol/hr}{7.2 \times 10^6\,L/hr} = 1.8 \times 10^{-3}\,M = \boxed{10^{-2.7}\,M = [NH_4Cl]_T}$$

HCO_3^-:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

$$= \frac{[HCO_3^-][H^+]}{10^{-6.35}} + [HCO_3^-] + \frac{10^{-10.33}[HCO_3^-]}{[H^+]}$$

$$= [HCO_3^-]\left(\frac{10^{-pH}}{10^{-6.35}} + 1 + \frac{10^{-10.33}}{10^{-pH}}\right)$$

$$[HCO_3^-] = C_T \Big/ \left(\frac{10^{-pH}}{10^{-6.35}} + 1 + \frac{10^{-10.33}}{10^{-pH}}\right) \;;\; C_T = 10^{-1.85}\,M.$$

CO_3^{2-}:

$$[CO_3^{2-}] = \frac{(10^{-10.33})[HCO_3^-]}{[H^+]} = (10^{pH-10.33})[HCO_3^-]$$

Now, use a spreadsheet to solve.

Fix $C_T = 10^{-1.85}\,M$; vary pH until $Alk = 10^{-1.8}\,M$. $\boxed{pH = 9.1}$

3c) Choose $C_T = 10^{-1.85}$ = 1.41E-02
Vary pH & solve for other unknown
components until Alk=$10^{-1.8}$, as desired.

Equations given on previous page.

pH	NH_3(aq)	[OH^-]	[HCO_3^-]	[CO_3^{2-}]	[H^+]	LOG(Alk)
9.35	1.17E-03	2.24E-05	1.28E-02	1.34E-03	4.47E-10	-1.779
9.3	1.11E-03	2.00E-05	1.29E-02	1.20E-03	5.01E-10	-1.784
9.25	1.05E-03	1.78E-05	1.30E-02	1.08E-03	5.62E-10	-1.789
9.2	9.98E-04	1.58E-05	1.31E-02	9.74E-04	6.31E-10	-1.793
9.15	9.40E-04	1.41E-05	1.32E-02	8.74E-04	7.08E-10	-1.798
9.1	8.83E-04	1.26E-05	1.33E-02	7.84E-04	7.94E-10	-1.802
9.12	9.06E-04	1.32E-05	1.33E-02	8.19E-04	7.59E-10	**-1.800**

3d) Vary pH until Alk=$10^{-1.86}$, as desired.

Eqns on next page.

pH	NH_3(aq)	[OH^-]	[HCO_3^-]	[CO_3^{2-}]	[H^+]	LOG(Alk)
10	0	1.00E-04	5.01E-02	2.34E-02	1.00E-10	-1.013
9.9	0	7.94E-05	3.98E-02	1.48E-02	1.26E-10	-1.158
9.8	0	6.31E-05	3.16E-02	9.33E-03	1.58E-10	-1.298
9.7	0	5.01E-05	2.51E-02	5.89E-03	2.00E-10	-1.432
9.6	0	3.98E-05	2.00E-02	3.72E-03	2.51E-10	-1.562
9.5	0	3.16E-05	1.58E-02	2.34E-03	3.16E-10	-1.687
9.4	0	2.51E-05	1.26E-02	1.48E-03	3.98E-10	-1.808
9.3	0	2.00E-05	1.00E-02	9.33E-04	5.01E-10	-1.925
9.36	0	2.29E-05	1.15E-02	1.23E-03	4.37E-10	**-1.855**

d) In region 3, we will have re-equilibrated with the atmosphere.

$pNH_3 = 0$ atm, then at equilibrium $NH_3(aq) = (K_{H,NH_3})(pNH_3) = 0$ atm,
e.g. all NH_3 produced escapes to the atmosphere,
and that quantity is not signifiant in relation to
the total atmosphere.

$CO_2(g)$ will also be equilibrated with the stream, so

$$[H_2CO_3^*] = (K_{H,CO_2})(pCO_2) = (10^{-1.46})(10^{-3.49}) = 10^{-4.95}\ M$$

To see how these changes affect alkalinity:

	H^+	H_2O	$H_2CO_3^*$	NH_4^+
$[CO_2]_T$	0	-1	1	
$[NH_3]_T$	-1			1

$$\Delta Alk = \Delta(-TOTH) = (+1)\Delta[NH_3] + (0)\Delta[CO_2]_T = \Delta[NH_3]$$

$\Rightarrow$ $CO_2(g)$ has no effect on alkalinity and
loss of NH_3 will decrease alk.

As all $NH_3(g)$ escapes to the atmosphere, $NH_4^+ \rightarrow NH_3(g) + H^+$ will
proceed to completion, so $\Delta NH_3(g) = -10^{-2.7}\ M$ (as calc'd
in part c).

$$Alk_3 = Alk_2 + \Delta Alk = 10^{-1.8} + (-10^{-2.7}) = 10^{-1.86}\ M.$$

$Alk = [NH_3(aq)] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$, as before

$[NH_3(aq)] = 0$

$[OH^-] = 10^{-14}/[H^+] = 10^{-14+pH}$

$$[HCO_3^-] = \frac{(10^{-6.35})[H_2CO_3^*]}{[H^+]} = \frac{10^{-6.35}\ 10^{-4.95}}{10^{-pH}} = 10^{-11.3}/10^{-pH}$$

$$[CO_3^{2-}] = \frac{(10^{-10.33})[HCO_3^-]}{[H^+]} = 10^{-21.6}/10^{-2pH}$$

Plug into Alk expression + solve for pH

$$\text{Alk} = 10^{-1.86} = [NH_3] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$$

$$= 0 + \frac{10^{-14}}{10^{-pH}} + \frac{10^{-11.3}}{10^{-pH}} + \frac{2(10^{-21.6})}{10^{-2pH}} - 10^{-pH}$$

Solving by varying pH to obtain the desired alkalinity, we find $pH = 9.36 = \boxed{9.4}$ (see spreadsheet)

We can also solve by assuming $[H^+] \ll [HCO_3^-], [CO_3^{2-}], [OH^-]$

Then

$$[H^+]^2 \text{Alk} = [H^+](10^{-14} + 10^{-11.3}) + 2(10^{-21.6})$$

$$0 = 10^{-1.86}[H^+]^2 + 10^{-11.3}[H^+] + 2\times10^{-21.6}$$

$$[H^+] = 4.4\times10^{-10} = 10^{-9.36}\ M$$

$$\boxed{pH = 9.4}$$

Alternate solution to Problem 3c using inferred recipe
(rather than Alkalinty)
Solution by A.G. Fitzmaurice (TA 2004)

c.) Species: H_2O, H^+, OH^-, $H_2CO_3^*$, HCO_3^-, CO_3^{2-}, NH_4^+, $NH_3(aq)$, Cl^-, Na^+

Tableau:

	H_2O	H^+	HCO_3^-	NH_4^+	Cl^-	Na^+
H_2O	1					
H^+		1				
OH^-	1	-1				
$H_2CO_3^*$		1	1			
HCO_3^-			1			
CO_3^{2-}		-1	1			
NH_4^+				1		
$NH_3(aq)$		-1		1		
Na^+						1
Cl^-					1	
$[H_2O]_T$	1					
$[NaHCO_3]_T$			1			1
$[Na_2CO_3]_T$		-1	1			2
$[NH_4Cl]_T$				1	1	

Mole Balances:

TOT H: $[H^+] - [OH^-] + [H_2CO_3^*] - [CO_3^{2-}] - [NH_3(aq)] = -[Na_2CO_3]_T$ (10)
TOT HCO_3: $[H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = [NaHCO_3]_T + [Na_2CO_3]_T$ (11)
TOT NH_4: $[NH_4^+] + [NH_3(aq)] = [NH_4Cl]_T$ (12)
TOT Cl: $[Cl^-] = [NH_4Cl]_T$ (13)
TOT Na: $[Na^+] = [NaHCO_3]_T + 2[Na_2CO_3]_T$ (14)

$[NH_3(aq)]$ can be calculated from Eq.(12) and the mass law expression:

$$10^{9.24-pH}[NH_3(aq)] + [NH_3(aq)] = [NH_4Cl]_T \tag{15}$$
$$[NH_3(aq)] = [NH_4Cl]_T / (10^{9.24-pH} + 1) \tag{16}$$

N.B. $[NH_4Cl]_T = (700kg/hr)(hr/3600s)(s/2m^3)(10^{-3}m^3/L)(10^3g/kg)(mol/63.5g) = 10^{-2.8}$

$$[NH_3(aq)] = 10^{-2.8} / (10^{9.24-pH} + 1) \tag{17}$$
$$[NH_4^+] = 10^{-2.8} - 10^{-2.8} / (10^{9.24-pH} + 1) \tag{18}$$

Using mass law expressions,

$$[H_2CO_3^*] = 10^{6.35-pH}[HCO_3^-] \tag{19}$$
$$[CO_3^{2-}] = 10^{pH-10.33}[HCO3^-] \tag{20}$$

Then Eq.(11) can be used to solve for $[HCO3^-]$:

$$10^{6.35\text{-}pH}\,[HCO_3^-] + [HCO_3^-] + 10^{pH\text{-}10.33}\,[HCO3^-] = 10^{-1.85} \tag{21}$$

$$[HCO_3^-](10^{6.35\text{-}pH} + 1 + 10^{pH\text{-}10.33}) = 10^{-1.85} \tag{22}$$

$$[HCO_3^-] = 10^{-1.85} / (10^{6.35\text{-}pH} + 1 + 10^{pH\text{-}10.33}) \tag{23}$$

These equations can be substituted into Eq.(10) and a solver can be employed to solve for pH:

pH ~ 9.13

d.) In Region 3, the ammonia species reach equilibrium with the atmosphere by leaving the system as in Region 1 since the partial pressure is 0. This is equivalent to the addition of $10^{-2.8}$ M HCl, so the alkalinity changes:

$$\begin{aligned} \text{Alk} &= [Na^+] - [Cl^-] \\ &= 10^{-1.81} - 10^{-2.8} \\ &= 10^{-1.85} \end{aligned} \tag{24}$$

Eq.(4), Eq.(9), Eq.(19), and Eq.(20) can be solved simultaneously to determine pH:

pH ~ 9.36

PROBLEM 4

$pH = 9.0$
$V_{sample} = 200\ mL$
$V_{H_2SO_4} = 24\ mL$ = Vol. required to titrate to CO_2 eq. pt. ($pH \approx 4.5$)
$[H_2SO_4] = 0.02\ N$

Assuming that only carbonate species are present,

$$Alk = C\text{-}Alk = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] = ?$$

Solve for Alk using the experimental data:

$$\text{mol } H^+ \text{ added} = \frac{0.02 \text{ mol } H^+}{L} \times 24\ \cancel{mL} \times \frac{L}{1000\ \cancel{mL}} = 4.8 \times 10^{-4} \text{ mol}$$

$$\frac{\text{mol Alk}}{L \text{ titrated sample}} = \frac{4.8 \times 10^{-4} \text{ mol}}{224\ \cancel{mL}} \times \frac{1000\ \cancel{mL}}{L} = 2.1 \times 10^{-3}\ M$$

M Alk original sample : $M_1 V_1 = M_2 V_2$

$$M_2 = \frac{M_1 V_1}{V_2} = \frac{(2.1 \times 10^{-3} M)(224 mL)}{(200 mL)} = 2.4 \times 10^{-3}\ M$$

$$\boxed{Alk = 2.4\ mEq/L = 2.4\ mM.}$$

Solve for $[HCO_3^-]$ in terms of Alk and pH:

$$Alk = -[H^+] + [OH^-] + [HCO_3^-] + \frac{2(10^{-10.33})[HCO_3^-]}{[H^+]}$$

$$= -[H^+] + \frac{K_w}{[H^+]} + [HCO_3^-]\left(1 + \frac{2(10^{-10.33})}{[H^+]}\right)$$

$$[HCO_3^-] = \frac{Alk + [H^+] - K_w/[H^+]}{\left(1 + \frac{2(10^{-10.33})}{[H^+]}\right)}$$; plug in $[H^+] = 10^{-9.0}$, $Alk = 2.4 \times 10^{-3} M$

$$[HCO_3^-] = 2.1855 \times 10^{-3}\ M$$

$$[CO_3^{2-}] = (10^{-10.33})[HCO_3^-]/[H^+] = 1.022 \times 10^{-4}\ M$$

Relative contributions to Alk (converted to %):

$[HCO_3^-]/Alk = 91.1\%$ $\frac{2[CO_3^{2-}]}{Alk} = 8.5\%$ $\frac{[OH^-]}{Alk} = 0.4\%$

$[H^+]/Alk = 4.2 \times 10^{-5}\%$ (insignificant)

PROBLEM 5

$CO_2(aq) + H_2O \rightleftharpoons CH_2O(aq) + O_2(aq)$

$K \gg K_{gas exchange}$

- no ΔAlk
- ΔC_T

a) $C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$ ✓

$Alk = 2.5mM = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$ ✓

$[HCO_3^-] + 2[CO_3^{2-}] = (2.5\times10^{-3}) - [OH^-] + [H^+]$; $[CO_3^{2-}] = \frac{10^{-10.33}[HCO_3^-]}{10^{-pH}}$

$[HCO_3^-](1 + 2\times10^{pH-10.33}) = 10^{-2.6} - 10^{-14+pH} + 10^{-pH}$

$$[HCO_3^-] = \frac{10^{-2.6} + 10^{-pH} - 10^{pH-14}}{(1+2\times10^{pH-10.33})}$$

$$[H_2CO_3^*] = \frac{[H^+][HCO_3^-]}{10^{-6.35}} = (10^{6.35-pH})[HCO_3^-]$$

$$[CO_3^{2-}] = (10^{pH-10.33})[HCO_3^-]$$

b) $Alk = 2.5mM = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$, assuming carbonate species are the only buffers present.

$$[HCO_3^-] + \frac{2(10^{-9.1})[HCO_3^-]}{10^{-pH}} = [H^+] - [OH^-] + (2.5\times10^{-3})$$

$$[HCO_3^-](1 + 2(10^{pH-9.1})) = 10^{-pH} - 10^{-14}/10^{-pH} + 10^{-2.6}$$

$$[HCO_3^-] = 10^{-2.6} + 10^{-pH} - 10^{pH-14} \Big/ (1 + 2\times10^{pH-9.1})$$

$$[H_2CO_3^*] = \frac{[H^+][HCO_3^-]}{10^{-6.0}} = (10^{6.0-pH})[HCO_3^-]$$

$$[CO_3^{2-}] = \frac{(10^{-9.1})[HCO_3^-]}{[H^+]} = (10^{pH-9.1})[HCO_3^-]$$

$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$

5) c) $B(OH)_3 + H_2O \leftrightharpoons \underset{8.7}{B(OH)_4^-} + H^+$ $\qquad \frac{[B(OH)_4^-][H^+]}{[B(OH)_3]} = 10^{8.7}$

at CO_2 eq. pt. (pH~4-5), $B(OH)_3$ is the major spps. to see the affect of $B(OH)_4^-$ on Alk:

	H_2O	H^+	$B(OH)_3$
$B(OH)_3$			1
$B(OH)_4^-$	1	-1	1

Then $Alk = C\text{-}Alk + [B(OH)_4^-] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + \underline{[B(OH)_4^-]} - [H^+]$

$$[B(OH)_4^-]_T = 0.4\,mM = 10^{-3.40} = [B(OH)_4^-] + [B(OH)_3]$$

$$10^{-3.40} = [B(OH)_4^-] + \frac{[B(OH)_4^-][H^+]}{10^{-8.7}}$$

$$10^{-3.40} = [B(OH)_4^-]\left(1 + \frac{10^{-pH}}{10^{-8.7}}\right)$$

$$[B(OH)_4^-] = 10^{-3.40}/(1 + 10^{8.7-pH})$$ ✓

Given $Alk = 2.5\,mM = 10^{-2.6}$

$$[HCO_3^-] + 2[CO_3^{2-}] = 10^{-2.6} - [B(OH)_4^-] - [OH^-] + [H^+]$$

$$[HCO_3^-] + 2\frac{(10^{-9.1})[HCO_3^-]}{10^{-pH}} = 10^{-2.6} - [B(OH)_4^-] - \frac{10^{-14}}{10^{-pH}} + 10^{-pH}$$

$$[HCO_3^-]\left(1 + 2(10^{pH-9.1})\right) = 10^{-2.6} + 10^{-pH} - 10^{pH-14} - [B(OH)_4^-]$$ ✓

$$[HCO_3^-] = \frac{10^{-2.6} + 10^{-pH} - 10^{pH-14} - [B(OH)_4^-]}{(1 + 2(10^{pH-9.1}))}$$

$$[CO_3^{2-}] = \frac{(10^{-9.1})[HCO_3^-]}{[H^+]} = (10^{pH-9.1})[HCO_3^-]$$

$$[H_2CO_3^*] = \frac{[H^+][HCO_3^-]}{10^{-6.0}} = (10^{6.0-pH})[HCO_3^-]$$

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

✓

5d)

Freshwater

pH	$[HCO_3^-]$	$[H_2CO_3]$	$[CO_3^{2-}]$	C_T
8.295	2.4644E-03	2.7972E-05	2.2736E-05	2.5152E-03
8.300	2.4639E-03	2.7645E-05	2.2995E-05	2.5145E-03
8.305	2.4634E-03	2.7323E-05	2.3256E-05	2.5139E-03

Seawater

pH	$[HCO_3^-]$	$[H_2CO_3]$	$[CO_3^{2-}]$	C_T
8.295	1.9111E-03	9.6890E-06	2.9942E-04	2.2202E-03
8.300	1.9058E-03	9.5516E-06	3.0205E-04	2.2174E-03
8.305	1.9005E-03	9.4160E-06	3.0469E-04	2.2146E-03

Seawater (including borate)

pH	$[B(OH)_4^-]$	$[HCO_3^-]$	$[H_2CO_3]$	$[CO_3^{2-}]$	C_T
8.295	1.1243E-04	1.8255E-03	9.2550E-06	2.8601E-04	2.1207E-03
8.300	1.1336E-04	1.8197E-03	9.1202E-06	2.8841E-04	2.1172E-03
8.305	1.1430E-04	1.8139E-03	8.9872E-06	2.9082E-04	2.1137E-03

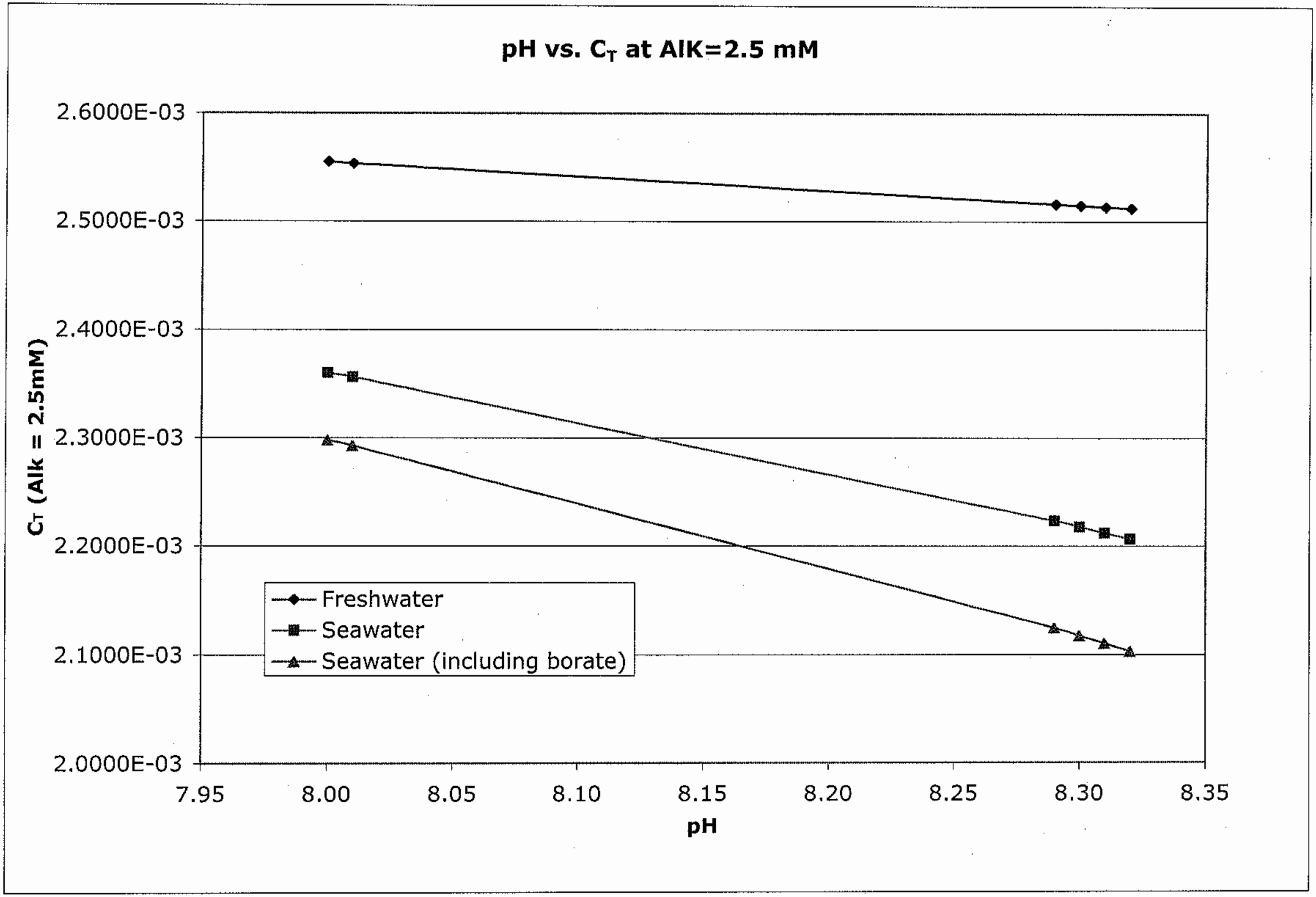
At $pH = 8.3 \pm 0.005$,

$C_{T,\text{fresh}}$ can be measured $\pm 6 \times 10^{-7} = 10^{-6.22}$ $= C_T(pH=8.305) - C_T(pH=8.300)$

$C_{T,\text{sw}}$ can be meas'd @ $\pm 2.8 \times 10^{-6} = 10^{-5.55}$

$C_{T,\text{sw,borate}}$ can be meas'd @ $\pm 3.5 \times 10^{-6} = 10^{-5.46}$

This is also shown in the plot, where the freshwater C_T vs. pH line has a smaller slope. The effect of pH on C_T is governed by pKa's of the carbonate system. In freshwater, $pKa_1 = 6.35$, $pKa_2 = 10.33$, both ≥ 1 pH unit away from $pH \approx 8.3$. In seawater, we are operating much closer to $pKa_2 = 9.1$, so changes in pH have a larger influence on C_T (when Alk = constant).



pH vs. C_T at AlK=2.5 mM