1.76 Aquatic Chemistry- Problem Set 1 Solutions

1. Book problem 1.2 a, f, g, i.

Recipe: $[Na_2SO_4]_T$= X $[H_2S]$=Y $[H_2O]$=55.4 M
Reactions: $H_20 = OH^- + H^+$; $H_2S = HS^- + H^+$; $HS^- = S^{2-} + H^+$
Spp: H_20, OH^-, H^+, H_2S, HS^-, S^{2-}, Na^+, SO_4^{2-}
components = # spp - # rxn: 8-3=5.
All choices have five components, so this condition is met.
For a proper component set, *each* species must be *uniquely* expressible in terms of the components.

1.2 a) a valid component set

	H_20	SO_4^{2-}	H_2S	Na^+	OH^-
H_20	1				
OH^-					1
H^+	1				-1
H_2S			1		
HS^-	-1		1		1
S^{2-}	-2		1		+2
SO_4^{2-}		1			
Na^+				1	

1.2 f) a valid component set

	H_20	SO_4^{2-}	H_2S	Na^+	S^{2-}
H_20	1				
OH^-	1		-1/2		1/2
H^+			1/2		-1/2
H_2S			1		
HS^-			1/2		1/2
S^{2-}					1
SO_4^{2-}		1			
Na^+				1	

1.2 g) These components are not independent. For example SO_4^{2-}= 1 Na_2SO_4 – 2 Na^+

1.2 i) a valid component set.

	H_20	H^+	O_2^o	Na^+	S^{2-}
H_20	1				
OH^-	1	-1			
H^+		1			
H_2S		2			1
HS^-		1			1
S^{2-}					1
SO_4^{2-}			2		1
Na^+				1	

2. River water…

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

2a)

Spp present at eq.: H_20, OH^-, H^+, H_2CO_3*, HCO_3^-, CO_3^{2-}, Cl^-, Na^+, Ca^{2+}, SO_4^{2-}, Mg^{2+}

Rxns to consider: $H_20 = OH^- + H^+$ $K_w=[OH^-][H^+]$ (1)
$H_2CO_3^* = HCO_3^- + H^+$ $K_{a1}=[HCO_3^-][H^+] / [H_2CO_3^*]$ (2)
$HCO_3^- = CO_3^{2-} + H^+$ $K_{a2}=[CO_3^{2-}][H^+] / [HCO_3^-]$ (3)

We do not consider these reactions:

$H_2SO_4 = HSO_4^- + H^+$, because H_2SO_4 is a strong acid, and dissociation is complete

$HSO_4^- = SO_4^{2-} + H^+$, because $HSO_4^- << SO_4^{2-}$ in solutions with pH > 2.9 (most of the systems in which we're interested. Except for maybe Eoghen…)

$HCO_3^- + OH^- = CO_3^{2-}$, because it is redundant. This K_{eq} expression can be derived from equations 1 and 3.

11spp – 3rxn = 8 components

	H_20	H^+	HCO_3^-	Na^+	Ca^{2+}	Cl^-	Mg^{2+}	SO_4^{2-}
H_20	1							
H^+		1						
OH^-	1	-1						
H_2CO_3*		1	1					
HCO_3^-			1					
CO_3^{2-}		-1	1					
Na^+				1				
Ca^{2+}					1			
Cl^-						1		
Mg^{2+}							1	
SO_4^{2-}								1
$[CO_2]_T$	-1	1	1					
$[NaCl]_T$				1		1		
$[CaSO_4]_T$					1			1
$[CaCO_3]_T$		-1	1		1			
$[MgCO_3]_T$		-1	1				1	
$[H_2O]_T$	1							

(1) TOT H: $[H^+] – [OH^-] + [H_2CO_3^*] – [CO_3^{2-}] = [CO_2]_T - [CaCO_3]_T - [MgCO_3]_T$
(2) TOT CO_2 (C_T): $[H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = [CO_2]_T + [CaCO_3]_T + [MgCO_3]_T$
(3) TOT Na: $[Na^+] = [NaCl]_T$

(4) TOT Ca: $[Ca^{2+}] = [CaSO_4]_T + [CaCO_3]_T$
(5) TOT Cl: $[Cl^-] = [NaCl]_T$
(6) TOT Mg: $[Mg^{2+}] = [MgCO_3]_T$
(7) TOT SO_4: $[SO_4^{2-}] = [CaSO_4]_T$
And… TOT H_2O (2a): $[H_2O] + [OH^-] = -[CO_2]_T + [H_2O]_T$

2b) Getting the electroneutrality equation from your Tableaux…

	H_20	H^+	NaCl	$CaSO_4$	$CaCO_3$	$MgCO_3$	CO_2	HCl
H_20	1							
H^+		1						
OH^-	1	-1						
$H_2CO_3^*$	1						1	
HCO_3^-	1	-1					1	
CO_3^{2-}	1	-2					1	
Na^+		1	1					-1
Ca^{2+}	-1	2			1		-1	
Cl^-		-1						1
Mg^{2+}	-1	2				1	-1	
SO_4^{2-}	1	-2		1	-1		1	
$[CO_2]_T$							1	
$[NaCl]_T$			1					
$[CaSO_4]_T$				1				
$[CaCO_3]_T$					1			
$[MgCO_3]_T$						1		
$[H_2O]_T$	1							

Our equations are now:

(8) TOTH: $[H^+] + [Na^+] + 2[Ca^{2+}] + 2[Mg^{2+}] – [OH^-] – [HCO_3^-] – 2[CO_3^{2-}] – [Cl^-] –2 [SO_4^{2-}] = 0$
This readily rearranges to the familiar form of the electroneutrality expression:
$[H^+] + [Na^+] + 2[Ca^{2+}] + 2[Mg^{2+}] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [Cl^-] + 2[SO_4^{2-}]$

(9) TOT Na: $[Na^+] = [NaCl]_T$
(10) TOT $CaSO_4$: $[SO_4^{2-}] = [CaSO_4]_T$
(11) TOT $CaCO_3$: $[Ca^{2+}] – [SO_4^{2-}] = [CaCO_3]_T$
(12) TOT $MgCO_3$: $[Mg^{2+}] = [MgCO_3]_T$
(13) TOT CO_2: $[H_2CO_3^*] + [HCO_3^-] + [SO_4^{2-}] + [CO_3^{2-}] - [Ca^{2+}] - [Mg^{2+}] = [CO_2]_T$
(14) TOT HCl: $-[Na^+] + [Cl^-] = 0$
TOTH(2b): $[H_2O] + [OH^-] + [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] – [Ca^{2+}] - [Mg^{2+}] + [SO_4^{2-}] = [H_2O]_T$

Verification that the sets of equations are equivalent:
(1) = (8) + (13) + (14) – (12) – (11)
(2) = (13) + (12) + (11)

(3) = (9)
(4) = (10) + (11)
(5) = (14) + (9)
(6) = (12)
(7) = (10)
(and TOTH (2a) = TOTH(2b) – (13))

2c) Equivalent solution with strong acids and bases…

From eqn (4), TOT Ca: $[Ca^{2+}] = [CaSO_4]_T + [CaCO_3]_T = 2.3 \times 10^{-3}$ M
Then for recipe 2c $[Ca^{2+}] = [Ca(OH)_2]_T = 2.3 \times 10^{-3}$ M $= 10^{-2.64}$ M

From eqn (3), TOT Na: $[Na^+] = [NaCl]_T = 1 \times 10^{-4}$ M
Then for recipe 2c $[Na^+] = [NaOH]_T = 1 \times 10^{-4}$ M

From eqn (5), TOT Cl: $[Cl^-] = [NaCl]_T = 1 \times 10^{-4}$ M
Then for recipe 2c $[Cl^-] = [HCl]_T = 1 \times 10^{-4}$ M

From equation (7), TOT SO_4: $[SO_4^{2-}] = [CaSO_4]_T = 3 \times 10^{-4}$ M
Then for recipe 2c $[SO_4^{2-}] = [H_2SO_4]_T = 3 \times 10^{-4}$ M $= 10^{-3.52}$ M

From eqn (6), TOT Mg: $[Mg^{2+}] = [MgCO_3]_T = 1 \times 10^{-3}$ M
Then for recipe 2, $[Mg^{2+}] = [Mg(OH)_2]_T = 1 \times 10^{-3}$ M

From eqn (2), TOT CO_2 (C_T): $[H_2CO_3^*]\ [HCO_3^-] + [CO_3^{2-}] = [CO_2]_T + [CaCO_3]_T + [MgCO_3]_T = (3 + 2 + 1) \times 10^{-3}$ M $= 6 \times 10^{-3}$ M
Then for recipe 2c, $[CO_2]_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = 6 \times 10^{-3}$ M $= 10^{-2.22}$ M

2d) More fun, except $[CO_2]_T = 5 \times 10^{-3}$ M.
Part a: The Tableau is unchanged (HCO_3^- is still the principle component, as adding this much CO_2 doesn't drop the pH below 6.3), so the equations remain the same. The amounts are higher:
$TOTH_{,new}$: $[H^+] - [OH^-] + [H_2CO_3^*] - [CO_3^{2-}] = [CO_2]_{T,new} - [CaCO_3]_T - [MgCO_3]_T = 2 \times 10^{-3}$ M
TOT $CO_{2,new}$: $[H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = [CO_2]_{T,\ new} + [CaCO_3]_T + [MgCO_3]_T = 8 \times 10^{-3}$ M

Part c: $[CO_2]_{T,\ new} = 8 \times 10^{-3}$ M; all other recipe amounts are the same.

2e) Bog sediment simulated by equilibration with $CO_2(g)$ and $H_2S(g)$.

As the system is open, we must chose H_2S and H_2CO_3* as components.

Now, we must consider the additional equilibria:

$H_2S\ (g) = H_2S\ (aq)$	$K_{H,H2S} = 10^{-0.99}$ M atm^{-1}
$H_2S\ (aq) = HS^- + H^+$	$K_{aH2S} = 10^{-7.02}$
$HS^- = S^{2-} + H^+$	$K_{a2,H2S} = 10^{-13.9}$
$CO_2(g) + H_2O = H_2CO_3*(aq)$	$K_{H,CO2} = 10^{-1.5}$ M atm^{-1}

Note: Can count X(g) as a species **and** $K_{H,X}$ expression as a rxn, or can count neither. (so # spp - # rxns = # components).

	H_20	H^+	H_2CO_3*	H_2S	Na^+	Ca^{2+}	Cl^-	Mg^{2+}	SO_4^{2-}
H_20	1								
H^+		1							
OH^-	1	-1							
H_2CO_3*			1						
HCO_3^-		-1	1						
CO_3^{2-}		-2	1						
H_2S				1					
HS^-		-1		1					
S^{2-}		-2		1					
Na^+					1				
Ca^{2+}						1			
Cl^-							1		
Mg^{2+}								1	
SO_4^{2-}									1
$[CO_2]_T$	-1		1						
$[H_2S]_T$				1					
$[NaCl]_T$					1		1		
$[CaSO_4]_T$						1			1
$[CaCO_3]_T$		-2	1			1			
$[MgCO_3]_T$		-2	1					1	
$[H_2O]_T$	1								

TOT H_2O: $[H_2O] + [OH^-] = -[CO_2]_T + [H_2O]_T$

TOT H: $[H^+] - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}] - [HS^-] - 2[S^{2-}] = -2\,[CaCO_3]_T - 2\,[MgCO_3]_T$

TOT CO_2 (C_T): $[H_2CO_3*] + [HCO_3^-] + [CO_3^{2-}] = [CO_2]_T + [CaCO_3]_T + [MgCO_3]_T$

TOTH2S: $[H_2S] + [HS^-] + [S^{2-}] = [H_2S]_T$

TOT Na: $[Na^+] = [NaCl]_T$

TOT Ca: $[Ca^{2+}] = [CaSO_4]_T + [CaCO_3]_T$

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

TOT Mg: $[Mg^{2+}] = [MgCO_3]_T$

TOT SO_4: $[SO_4^{2-}] = [CaSO_4]_T$

$[CO_2]_T$ is irrelevant here because the concentration of dissolved $CO_2(aq)$ (H_2CO_3*) is controlled by the equilibration with $CO_2(g)$ and the pH of the solution (not the initial CO_2 of the system).

3. Log C v. pH Diagrams.
For the system described in 2a:

First, we'll derive the equations for the log C v. pH diagram. Na^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, and Cl^- do not need to appear on your diagram because they are constant, not a function of pH.

We showed in 2a that
$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = [CO_2]_T + [CaCO_3]_T + [MgCO_3]_T = 6\times10^{-3}\ M = 10^{-2.2}\ M$

The assumptions that we make are pH dependent, so we must develop piece-wise defined equations for each pH range.

For pH<6.3, $[H_2CO_3^*] >> [HCO_3^-], [CO_3^{2-}]$,
so $[H_2CO_3^*] \approx C_T \approx 10^{-2.2}$ M.

$[HCO_3^-] = K_{a1}[H_2CO_3^*]/[H^+]$ (a rearrangement of K_{a1})
$\log [HCO_3^-] = \log K_{a1} + \log[H_2CO_3^*] - \log[H^+]$
$\log [HCO_3^-] = -6.3 - 2.2 + pH$
$= -8.5 + pH$ (a straight line with a slope of +1)!

$[CO_3^{2-}] = K_{a2}[HCO_3^-]/[H^+]$ (a rearrangement of K_{a2}. you could use K_{a1} to replace $[HCO_3^-]$ or you could proceed as follows)
$\log [CO_3^{2-}] = \log K_{a2} + \log [HCO_3^-] - \log[H^+]$ (Now plug in your eqn for $\log [HCO_3^-]$)
$\log [CO_3^{2-}] = \log K_{a2} + \log K_{a1} + \log[H_2CO_3^*] - \log[H^+] - \log[H^+]$
$\log [CO_3^{2-}] = -10.3 - 6.3 - 2.2 + pH + pH$
$\log [CO_3^{2-}] = -18.8 + 2pH$ (a straight line with a slope of +2)!

For pH = 6.3, $[HCO_3^-] = K_{a1}[H_2CO_3^*]/[H^+] = 10^{-6.3}[H_2CO_3^*]/10^{-6.3}$
$[HCO_3^-] = [H_2CO_3^*]$

For 6.3<pH<10, $[HCO_3^-] >> [H_2CO_3^*], [CO_3^{2-}]$,
so $[HCO_3^-] \approx C_T \approx 10^{-2.2}$ M.

Rearrange K_{a1} and take the log of both sides to find:
$\log[H_2CO_3^*] = -\log K_{a1} + \log [HCO_3^-] + \log[H^+]$
$\log[H_2CO_3^*] = +6.3 - 2.2 - pH = 4.1 - pH$ (a line with a slope of –1)!

Use K_{a2} to find:
$\log[CO_3^{2-}] = \log K_{a2} + \log [HCO_3^-] - \log[H^+]$
$\log[CO_3^{2-}] = -10.3 - 2.2 + pH = -12.5 + pH$

For pH = 10.3, $[HCO_3^-] = [CO_3^{2-}]$

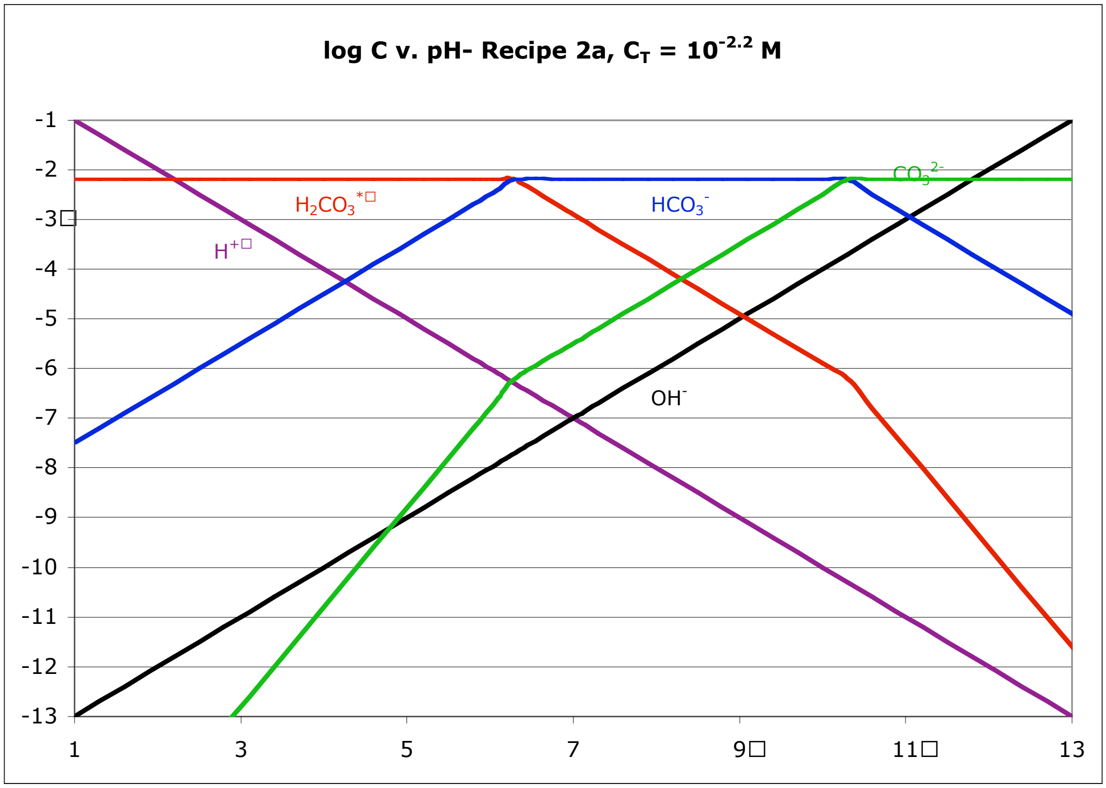
For pH>10.3, $[CO_3^{2-}] >> [H_2CO_3^*], [HCO_3^-]$

so $[CO_3^{2-}] \approx C_T \approx 10^{-2.2}$ M.

$\log [HCO_3^-] = \log [CO_3^{2-}] - \log K_{a2} + \log[H^+] = -2.2 + 10.3 - pH = 8.1 - pH$

$\log[H_2CO_3^*] = \log [CO_3^{2-}] - \log K_{a2} - \log K_{a1} + \log[H^+] + \log[H^+]$
$\log[H_2CO_3^*] = -2.2 + 10.3 + 6.3 - 2pH = 14.4 - 2pH$

For all pH:
$\log[H^+] = -pH$
$\log[OH^-] = \log K_w - \log[H^+] = -14 + pH$



Note: These look a lot better when done by hand… You should be able to do these by hand.

Now, use TOTH & the graph to solve for pH:
TOTH (from 2a): $[H^+] - [OH^-] + [H_2CO_3^*] - [CO_3^{2-}] = [CO_2]_T - [CaCO_3]_T - [MgCO_3]_T = 0$
The possible solutions are:

1. $[H^+] = [OH^-]$; $[H^+], [OH^-] >> [H_2CO_3^*], [CO_3^{2-}]$
2. $[H^+] = [CO_3^{2-}]$, $[H^+], [CO_3^{2-}] >> [OH^-], [H_2CO_3^*]$
3. $[H_2CO_3^*] = [OH^-]$, $[H_2CO_3^*], [OH^-] >> [CO_3^{2-}], [H^+]$
4. $[H_2CO_3^*] = [CO_3^{2-}]$, $[H_2CO_3^*], [CO_3^{2-}] >> [OH^-], [H^+]$

The only valid solution is (4), so $[H_2CO_3^*] = [CO_3^{2-}]$. Using K_{a1} and K_{a2} we find,
$([H^+][HCO_3^-]/K_{a1}) = (K_{a2}[HCO_3^-]/[H^+])$
$[H^+]^2 = [HCO_3^-]*K_{a1}*K_{a2}/[HCO_3^-]$
$[H^+]^2 = K_{a1}*K_{a2} = 10^{(-6.3-10.3)} = 10^{-16.6}$

$[H^+]=10^{-8.3}$ M, **pH = 8.3**

For the system described in 2d)
The log C vs. pH plot is the same, except that $C_T = 8 \times 10^{-3}$ M $= 10^{-2.09}$ M. The intersecting points of the species occur at the same pHs, the slopes are the same, but the plot of the carbonate species are shifted up on the y-axis to the higher C_T value.

We can use the same plot to solve for the pH. Recall, we showed
TOTH:$[H^+]–[OH^-]+[H_2CO_3^*]–[CO_3^{2-}]=[CO_2]_{T,new}-[CaCO_3]_T-[MgCO_3]_T=2\times10^{-3}M= 10^{-2.7}$ M

The possible solutions are:

1. $[H^+]=10^{-2.7}$ M, and $[H^+]>>[OH^-],[H_2CO_3^*],[CO_3^{2-}]$
2. $[H_2CO_3^*]= 10^{-2.7}$ M, and $[H_2CO_3^*]>>[OH^-],[CO_3^{2-}],[H^+]$

(2) is a valid solution, so $[H_2CO_3^*]= 10^{-2.7}$ M.
Recall from 2d, TOT $CO_{2,new}$:$[H_2CO_3^*] +[HCO_3^-]+ [CO_3^{2-}] = 8\times10^{-3}$ M $= 10^{-2.09}$ M

Assume $[HCO_3^-] >> [CO_3^{2-}]$ (a valid assumption when pH<10.3).
Then, $[H_2CO_3^*] +[HCO_3^-]= 10^{-2.09}$ M
$[HCO_3^-]= 10^{-2.09}$ M $-[H_2CO_3^*] = 10^{-2.09}$ M $-10^{-2.7}$ M $= 6 \times 10^{-3}$ M $=10^{-2.2}$ M

From K_{a1}, $[H^+] = K_{a1}[H_2CO_3^*]/[HCO_3^-] = (10^{-6.3})(10^{-2.7})/(10^{-2.2}) = 10^{-6.8}$ M.
pH=6.8

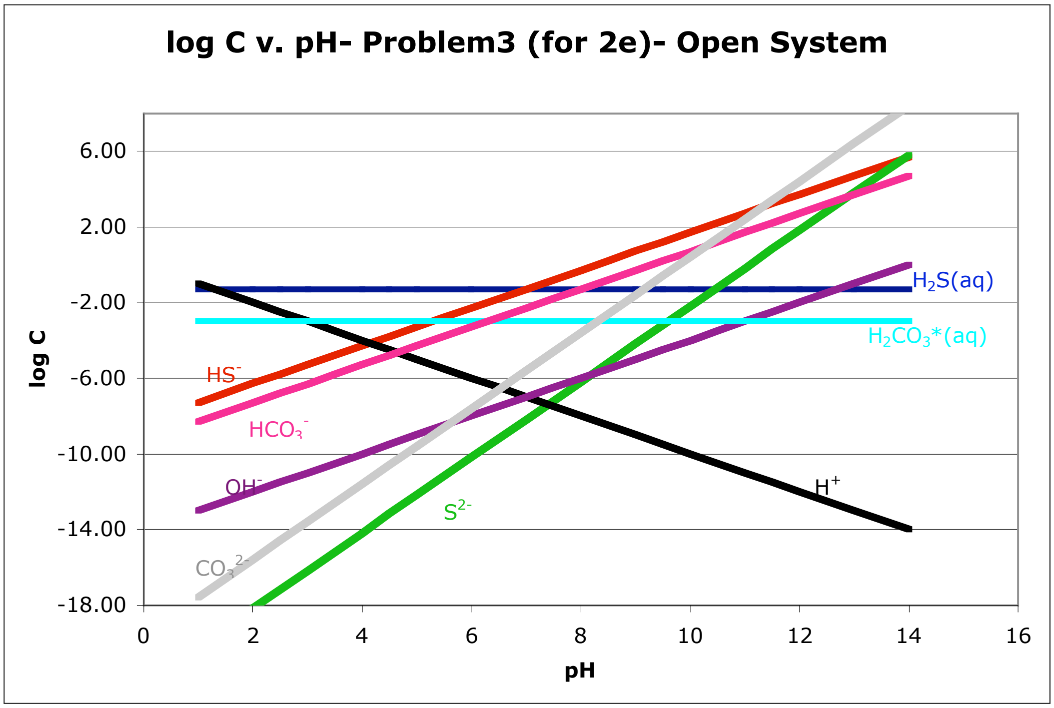
For the system described in 2e)

This is an open system. The amount of dissolved species of the equilibrated gas will be controlled by Henry's Law. We will develop the equations for H_2S; the equations for the carbonate system are analogous.

As $K_{H,H2S} = 10^{-0.99}$ M atm^{-1} = H_2S (aq)/ H_2S (g)
H_2S (aq) = (pH_2S (g)) $K_{H,H2S}$
=(0.5 atm) ($10^{-0.99}$ M atm^{-1})
H_2S (aq) = $10^{-1.29}$ M (a straight line independent of pH)!!

From $K_{aH2S} = 10^{-7.02}$,
$\log [HS-] = \log K_{aH2S} + \log [H_2S (aq)] –\log[H+]$
$= -7.02 –1.29 +pH = -8.31 + pH$

From $K_{a2,H2S} = 10^{-13.9}$,
$\log [S^{2-}] = \log K_{a2,H2S} + \log [HS-] –\log[H+]$
$\log [S^{2-}] = \log K_{a2,H2S} + \log K_{aH2S} + \log [H_2S (aq)] –2\log[H+]$
$= -13.9 -7.02 –1.29 +2pH = -22.2 + 2pH$



Use TOTH and the plot to solve the pH of the system:

TOT H: $[H^+] – [OH^-] -[HCO_3^-] – 2[CO_3^{2-}] – [HS^-] – 2[S^{2-}]= -2\ [CaCO_3]_T\ -2\ [MgCO_3]_T = -10^{-2.2}$ M

Possible solutions:

(1) $– [OH^-] = -10^{-2.2}$ M, other spp. negligible
(2) $-[HCO_3^-] = -10^{-2.2}$ M, other spp. negligible
(3) $– 2[CO_3^{2-}] = -10^{-2.2}$ M, other spp. negligible
(4) $– [HS^-] = -10^{-2.2}$ M, other spp. negligible
(5) $– 2[S^{2-}]= -10^{-2.2}$ M, other spp. negligible

(4) is a valid solution, so $[HS^-] = 10^{-2.2}$ M

$[H^+]= (K_{aH2S})[H_2S\ (aq)]/[HS^-] = (10^{-7.02})(10^{-1.29})/(10^{-2.2}) = 10^{-6.1}$ M

pH = 6.1, and we can see from the graph that the other spp. in the TOTH equation where negligible, so our assumption holds.

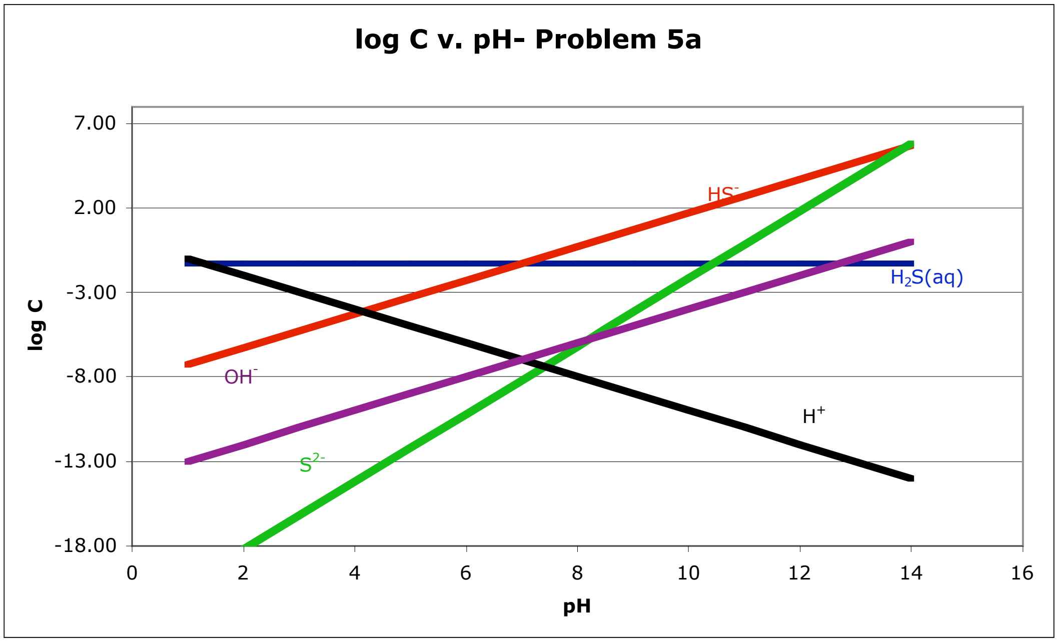
4.Open system.

4a) $[H_2S] = K_{H,H2S} * pH_2S = (10^{-0.99}\ M\ atm^{-1})*(10^{-0.30}\ atm) = 10^{-1.29}\ M = 0.051\ M$
This is independent of pH, so at pH 5,7,9, $[H_2S] = 10^{-1.29}\ M = 0.051\ M$

We can rearrange the equilibrium expressions to find:
$[HS^-] = (K_{a1})\ [H_2S]/[H^+]$ (1)
$[S^{2-}] = (K_{a2})[HS^-]/\ [H^+]$ (2) (Plug 1 into 2 to find):
$[S^{2-}] = (K_{a2})(K_{a1})[H_2S]/[H^+]^2$

pH	$[HS^-]$ (M)	$[S^{2-}]$ (M)
5	$5.1 \times 10^{-4} = 10^{-3.29}$	$6.4 \times 10^{-13} = 10^{-12.2}$
7	$5.1 \times 10^{-2} = 10^{-1.29}$	$6.4 \times 10^{-9} = 10^{-8.2}$
9	$5.1 = 10^{0.71}$	$6.4 \times 10^{-5} = 10^{-4.2}$

The equations for this plot were derived in problem 3.



4b) Recipe: $[H_2S]_T$ + $[H_2O]_T$

Reactions: $H_20 = OH^- + H^+$ $Kw = [OH^-][H^+] = 10^{-14}$

$H_2S = HS^- + H^+$ $K_{a1} = [HS^-][H^+]/[H_2S] = 10^{-7.02}$

$HS^- = S^{2-} + H^+$ $K_{a2} = [S^{2-}][H^+]/[HS^-][] = 10^{-7.02}$

Spp: H_20, OH^-, H^+, H_2S, HS^-, S^{2-}

6 spp – 3 rxns = 3 components

	H_2O	H^+	HS^-
H_2O	1		
OH^-	1	-1	
H^+		1	
H_2S		1	1
HS^-			1
S^{2-}		-1	1
$[H_2O]_T$	1		
$[H_2S]_T$		1	1

	H_2O	H^+	H_2S
H_2O	1		
OH^-	1	-1	
H^+		1	
H_2S			1
HS^-		-1	1
S^{2-}		-2	1
$[H_2O]_T$	1		
$[H_2S]_T$			1

The Tableau on the left gives two equations (TOTH and TOTHS-) that are equal to $[H_2S]_T$; an unknown quantity. Thus, these equations are not very useful.

The Tableau on the right gives only one equation (TOT H2S) that is equal to $[H_2S]_T$. We want to minimize the number of useless equations, so it is wise to choose the dissolved species of the equilibrated gas as a component. Additionally, the TOTH eqn is equal to a known quantity in this case- fantastic!

TOTH: $[H^+] - [OH^-] - [HS^-] - 2[S^{2-}] = 0$

So $[H^+] = [OH^-] + [HS^-] + 2[S^{2-}]$

The possibilities are:

1) $[H^+] = [OH^-]$ and $[H^+], [OH^-] >> [HS^-], [S^{2-}]$:

BUT… when $[H^+] = [OH^-]$, $[H^+], [OH^-] << [HS^-]$, so this is not the solution.

2) $[H^+] = 2[S^{2-}]$ and $[H^+], [S^{2-}] >> [OH^-], [HS^-]$

BUT… when $[H^+] = [S^{2-}]$, $[H^+], [S^{2-}] << [OH^-], [HS^-]$, so this is not the solution.

3) $[H^+] = [HS^-]$ and $[H^+], [HS^-] >> [OH^-], [S^{2-}]$… ah ha! There is a place on the plot where this is true, and it looks like it's around pH = 4.1.

We can find the true pH using the TOTH equation, the assumptions in (3), K_H and K_{a1}:

$[H^+] = [HS-] = (K_{a1})[H_2S]/[H^+]$

$[H^+]^2 = (K_{a1})(K_{H,H2S})(0.5 \text{ atm}) = (10^{-7.02})(10^{-0.99})(10^{-0.3}) = (10^{-8.31})$

pH=4.1_6 (This subscript means that the subscripted digit is insignificant).

It remains to show that our assumptions hold by plugging pH into the appropriate eqns:

$[HS^-] = (K_{a1})[H_2S]/[H^+] = 10^{-4.1}$ M

$[OH^-] = Kw/[H^+] = 10^{-9.8}$ M

$[S^{2-}] = (K_{a2})(K_{a1})[H_2S]/[H^+]^2 = 10^{-13.9}$ M

So the assumption $[H^+], [HS^-] >> [OH^-], [S^{2-}]$ holds!

4c) adding NaOH.
Adding base, we expect the pH to increase.

	H_2O	H^+	H_2S	Na^+
H_2O	1			
OH^-	1	-1		
H^+		1		
H_2S			1	
HS^-		-1	1	
S^{2-}		-2	1	
Na^+				1
$[H_2O]_T$	1			
$[H_2S]_T$			1	
$[NaOH]_T$	1	-1		1

The new TOTH:
$[H^+] – [OH^-] –[HS^-] –2[S^{2-}] = -[NaOH]_T = -10^{-2.3}$ M

The possible solutions are:
1) $– [OH^-] = - 10^{-2.3}$ M; $[OH^-] >> [HS^-],[S^{2-}], [H^+]$
2) $– [HS^-] = - 10^{-2.3}$ M; $[HS^-]>> [OH^-],[S^{2-}], [H^+]$
3) $– 2[S^{2-}] = - 10^{-2.3}$ M; $[S^{2-}] >>[OH^-],[HS^-],[H^+]$

There is a point on the graph where # 2 is true, so we can solve #2 for $[H^+]$:
$[HS^-] = 10^{-2.3}$ M $= (K_{a1}) [H_2S]/[H^+]$
$[H^+]= (K_{a1}) [H_2S]/[HS^-]= 10^{-5.99}$ M, **pH ≈6.0**

4d) adding HNO_3. Adding acid, we expect the pH to decrease.

	H_2O	H^+	H_2S	NO_3^-
H_2O	1			
OH^-	1	-1		
H^+		1		
H_2S			1	
HS^-		-1	1	
S^{2-}		-2	1	
NO_3^-				1
$[H_2O]_T$	1			
$[H_2S]_T$			1	
$[HNO_3]_T$	1	1		1

The new TOTH:
$[H^+] – [OH^-] –[HS^-] –2[S^{2-}] = [HNO_3]_T = 10^{-3}$ M

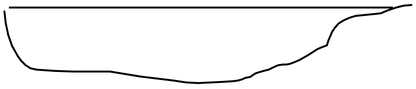
The only possible solution is
$[H^+] = 10^{-3}$ M**, so pH = 3.0**

5. Open v. Closed. (Answer from Linda Kalnejais' solutions, 2001).

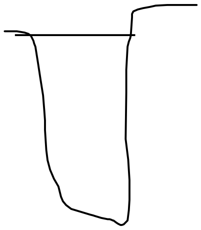
A closed system cannot exchange matter with its surroundings. In an open system, there is free exchange of materials across the boundaries of the system. For example, gas exchange across a water-air interface or precipitation/ dissolution of a solid phase represent material fluxing between a system and its surroundings.

Some things to assess if a lake can be modeled as an open system:

- What is the surface area: volume (SA:V) ratio of the lake?



high SA:V



low SA:V

A high SA:V ratio facilitates gas exchange, whereas a low ratio acts to isolate deeper waters.

- Is the lake well-mixed or is it stratified? If the lake is stratified the lower layers are somewhat isolated and so a closed system model may be appropriate.

- Is the lake sheltered? Gas exchange may be restricted if there is not much wind blowing over the lake

- Is there input/output of material from the sediments?

- What are the timescales of the reactions I am interested in, and how do they compare to the timescales of gas exchange or precipitation etc? If the timescales of exchange are much greater than those of interest, transfer of material is the slow process, so a closed model is appropriate.