Homework #8

1. Prepare a complete Log C vs pH diagram for a system containing pure water and an excess of α-aluminum hydroxide (25°C and I=0). (2 points)

Use the equilibrium constants in Stumm & Morgan's Table A6.1 (after page 324 in the 3rd edition) or the values in the tables on pgs 241 and 242 in the 2nd edition (see table below). Show how you determined the equations for each of the lines.

Equilibrium Data

Species	Equilibrium	Log K	
		Benjamin[1]	Stumm & Morgan[2]
$Al(OH)_3$	$Al(OH)_3 = Al^{+3} + 3OH^-$	-33.23	-33.5
$AlOH^{+2}$	$Al^{+3} + OH^- = Al(OH)^{+2}$	9.01	9.0
$Al(OH)_2^+$	$Al^{+3} + 2OH^- = Al(OH)_2^+$	17.90	18.7
$Al(OH)_3^o$	$Al^{+3} + 3OH^- = Al(OH)_3^o$	26.00	27.0
$Al(OH)_4^-$	$Al^{+3} + 4OH^- = Al(OH)_4^-$	33.00	33.0
$Al_3(OH)_4^{+5}$	$3Al^{+3} + 4OH^- = Al_3(OH)_4^{+5}$		42.1
$Al_{13}O_4(OH)_{24}^{+7}$	$13Al^{+3} + 32OH^- = Al_{13}O_4(OH)_{24}^{+7} + 4H_2O$		349.3

Solution to #1

LogC vs pH Line Summary

Species	Slope	Intercept	
		Benjamin[3]	Stumm & Morgan[4]
Al^{+3}	-3	8.77	8.5

[1] Table 8.7 for Kso, Table 8.2 for hydroxide complexes
[2] Table A6.1 in 3rd edition, following page 324
[3] Table 8.7 for Kso, Table 8.2 for hydroxide complexes
[4] Table A6.1 in 3rd edition, following page 324

$AlOH^{+2}$	-2	3.78	3.5
$Al(OH)_2^+$	-1	-1.33	-0.8
$Al(OH)_3^o$	0	-7.23	-6.5
$Al(OH)_4^-$	+1	-14.23	-14.5
$Al_3(OH)_4^{+5}$	-5		11.6
$Al_{13}O_4(OH)_{24}^{+7}$	-7		11.8

Using the equilibria, algebraic manipulation gets us:

$$\text{Log}[Al^{+3}] = 8.5 - 3pH$$

$$\text{Log}[AlOH^{+2}] = 3.5 - 2pH$$

$$\text{Log}[Al(OH)_2^+] = -0.8 - pH$$

$$\text{Log}[Al(OH)_3^0] = -6.5$$

$$\text{Log}[Al(OH)_4^-] = -14.5 + pH$$

$$\text{Log}[Al_3(OH)_4^{+5}] = 11.6 - 5pH$$

$$\text{Log}[Al_{13}O_4(OH)_{24}^{+7}] = 11.8 - 7pH$$

Now plot these lines on a logC vs pH axis. See diagram below:

2. Determine the pH of this solution. **(1 point)**

Solution to #2

Use ENE

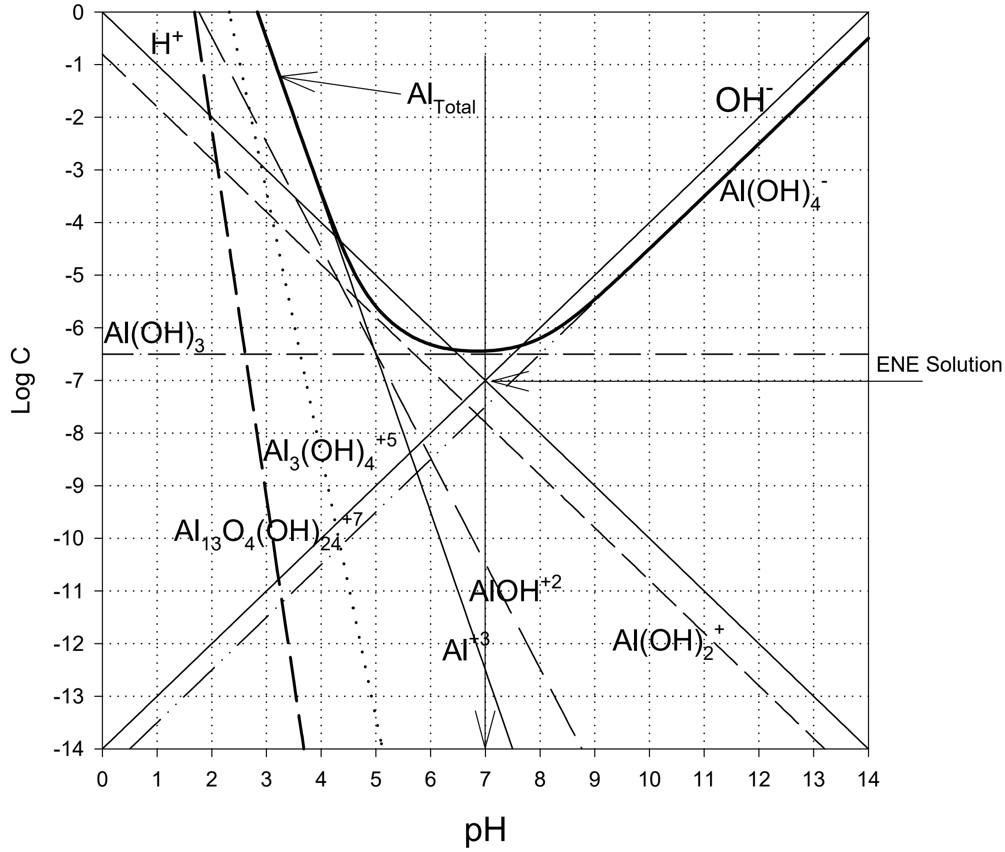
$3[Al^{+3}] + 2[AlOH^{+2}] + [Al(OH)_2^+] + 5[Al_3(OH)_4^{+5}] + 7[Al_{13}O_4(OH)_{24}^{+7}] + [H^+] = [OH^-] + [Al(OH)_4^-]$

Make simplifying assumptions to end up with:

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

Which with the help of the solubility graph gives us:

pH = 7.0



3. Determine the pH of a 0.1 mM solution of alum (aluminum sulfate). **(1 point)**

Solution to #3

Use ENE, this time including sulfate

$3[Al^{+3}] + 2[AlOH^{+2}] + [Al(OH)_2^{+}] + 5[Al_3(OH)_4^{+5}] + 7[Al_{13}O_4(OH)_{24}^{+7}] + [H^{+}] = [OH^{-}] + 2[SO_4^{-2}] + [Al(OH)_4^{-}]$

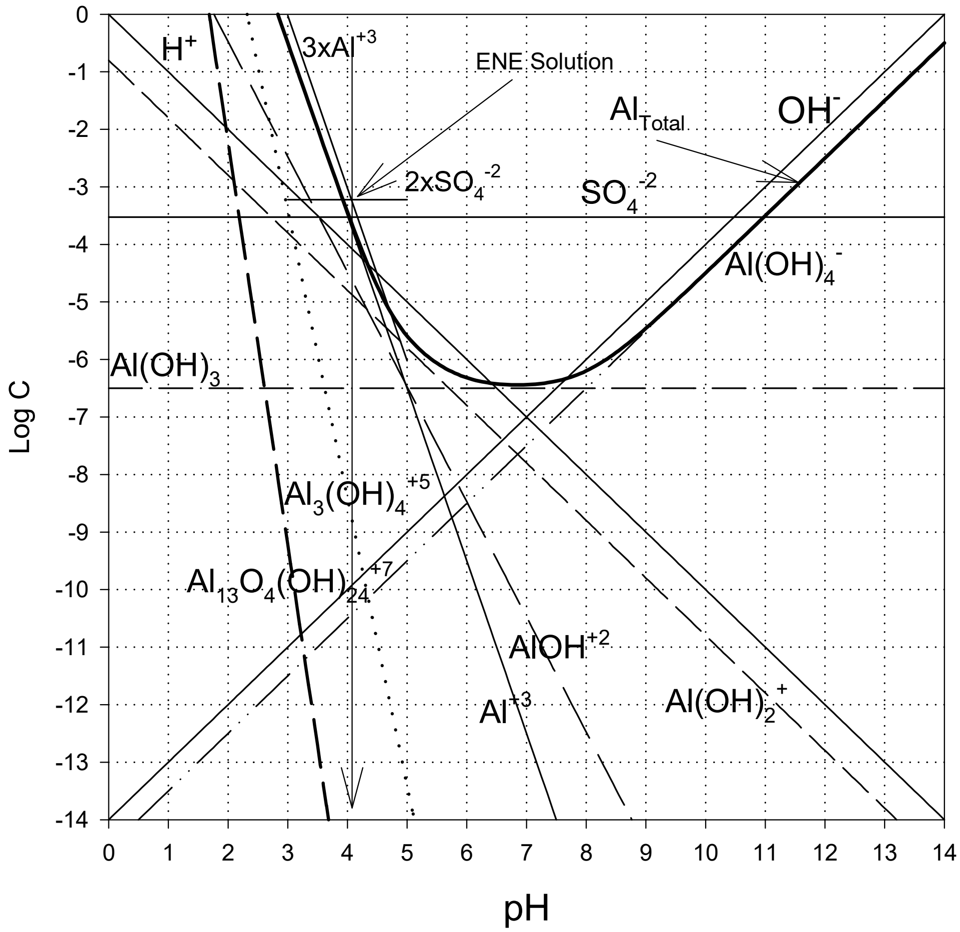
Make simplifying assumptions to end up with:

$$3[Al^{+3}] = 2[SO_4^{-2}]$$

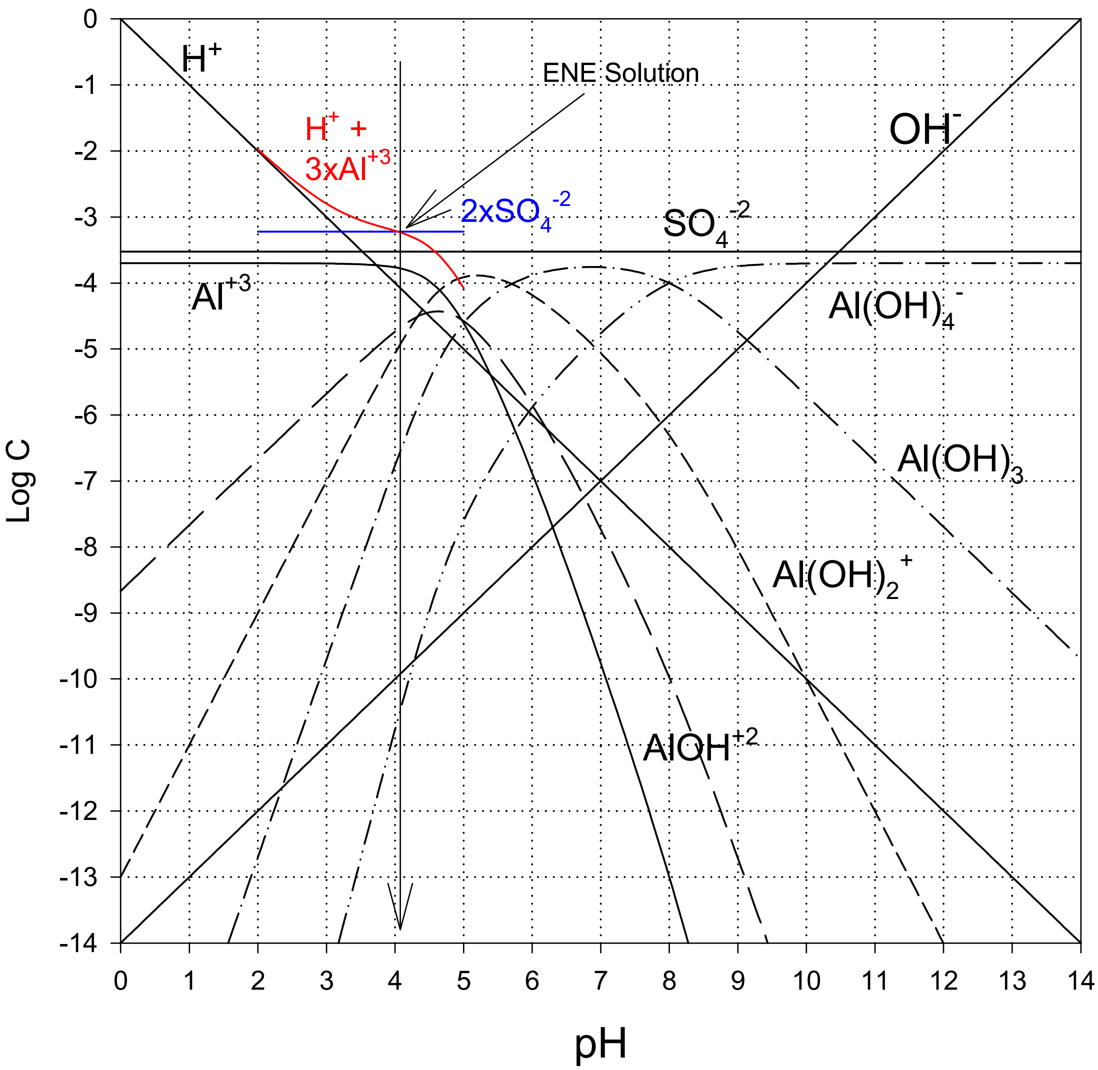
Which with the help of the solubility graph gives us:

$$pH = 4.1$$

you may recognize that at this pH our implicit assumption that the system is in equilibrium with aluminum hydroxide solid is on the verge of being invalid (we will have $2x10^{-4}$M total Al). Its pretty close, and even if we don't have the solid phase, this doesn't change our answer very much because all of the Al species will retain the same relative concentrations (i.e., Al^{+3} will be dominant at these low pHs)



Assuming that there is no precipitate, you can re-draw the diagram as follows. Note that you get essentially the same answer.


H+
ENE Solution
H+ +
3xAl+3
2xSO4-2
SO4-2
OH-
Al+3
Al(OH)4-
Al(OH)3
Al(OH)2+
AlOH+2
Log C
pH
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14