CEE 680 16 April 2015

SECOND EXAM

Closed book, two pages of notes allowed.

Answer any two of the three questions. Please state any additional assumptions you made, and show all work.

Some useful constants:	$P_{CO2} = 10^{-3.5}$ atm $K_H = 10^{-1.5}$ M/atm

1. Carbonate System.

(50% for all three parts) Two raw drinking waters are mixed as they enter the headworks of a water treatment plant. The two are characterized as follows:

Water	Flow (MGD)	Alkalinity (mg/L as CaCO3)	pH
#1	20	5	6.30
#2	10	275	8.85

A. What will the pH of the blended water be immediately after mixing?

B. What will the pH of the blended water be after it has reached equilibrium with the bulk atmosphere?

C. How many mg/L of caustic soda (NaOH) must be added to the unequilibrated blended water in part "A" to raise the pH to 9.80 ?

2. Complexation

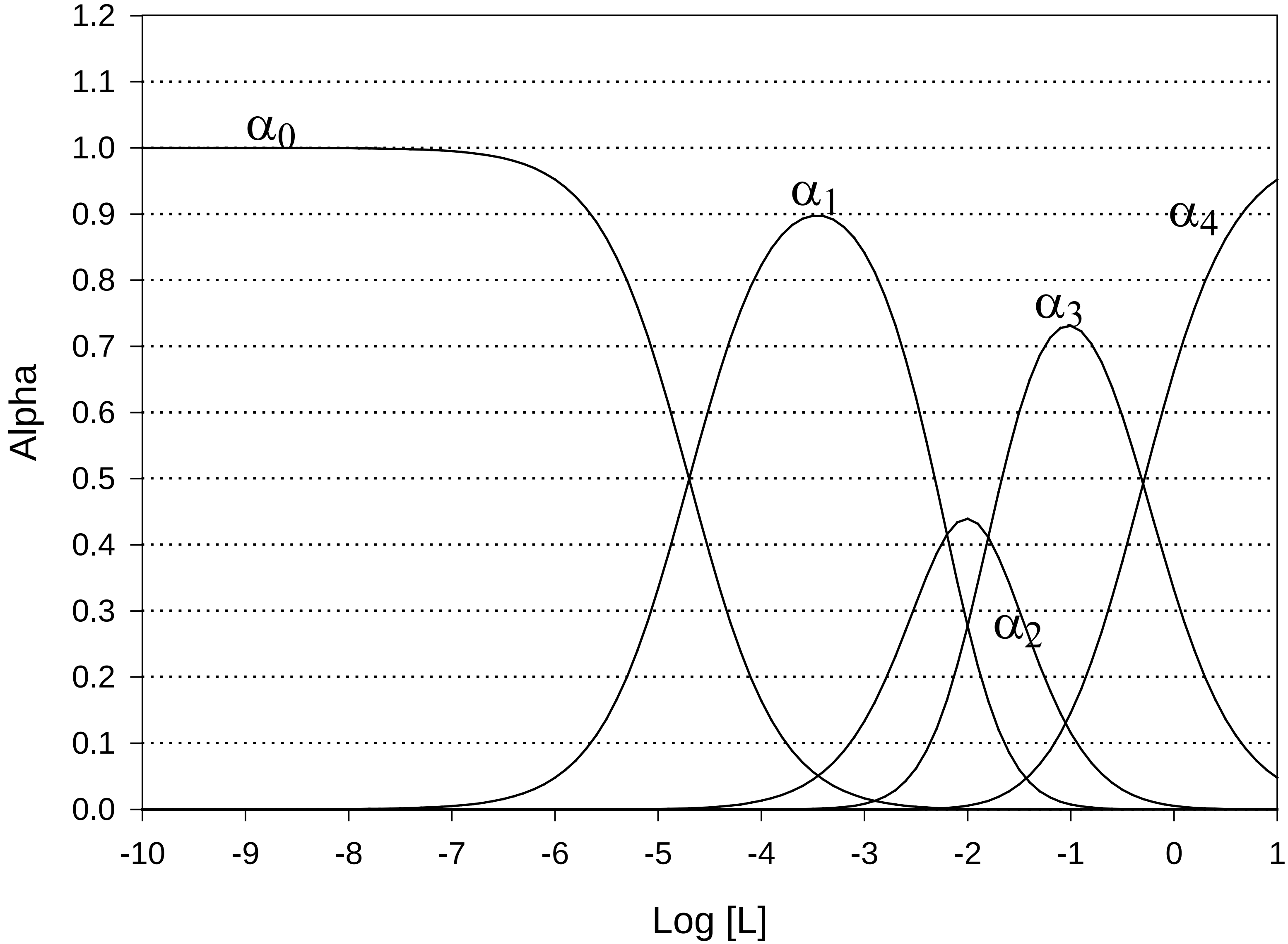
(50% total for all 4 parts) Bromide forms few strong complexes. Silver is one exception. The following two part problem concerns complexes of this metal-ligand combination.

A. (25%) Below is an "accurate" alpha graph for the Ag^{+} – Br^{-} system. Using this graph determine the complete speciation in a waste brine where the total silver concentration is 2 mM and the total bromide concentration is 10 mM. Assume the pH of the brine is low enough to render any hydroxide complexes insignificant.

B. (10%) Now explain in qualitative terms how the speciation would change if the brine wastewater pH was substantially elevated so that hydroxide complexes became important and justify your answer using your knowledge of water chemistry

C. (10%) Finally explain in qualitative terms how the speciation would change if the groundwater pH remained low, but if 10 mM of Hg^{+2} was added. Note that Hg^{+2} is another metal ion that strongly complexes bromide. Again, justify your answer using your knowledge of water chemistry.

D. (5%) Finally explain in qualitative terms how the speciation would change if you took into account the impacts of high ionic strength. Note that the alpha graph as shown is based on the idea infinite dilution case (i.e., no ionic strength). Again, justify your answer using your knowledge of water chemistry.



1.2
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Alpha
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α_1
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-4
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-2
-1
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1
Log [L]

3. pH, metals and lake liming

(50 % for all 3 parts) There are many lakes in NY and New England that are naturally acidic and impacted by acid precipitation. One of these is Lake Alcoa. This popular vacation spot now has a pH of 4.7, an alkalinity of -0.95 mg/L, and a total carbonate concentration (C_T) of $5x10^{-5}$ M (assume 25°C, ~0 ionic strength). Local officials have proposed lime {$Ca(OH)_2$} as a solution to the low pH problem.

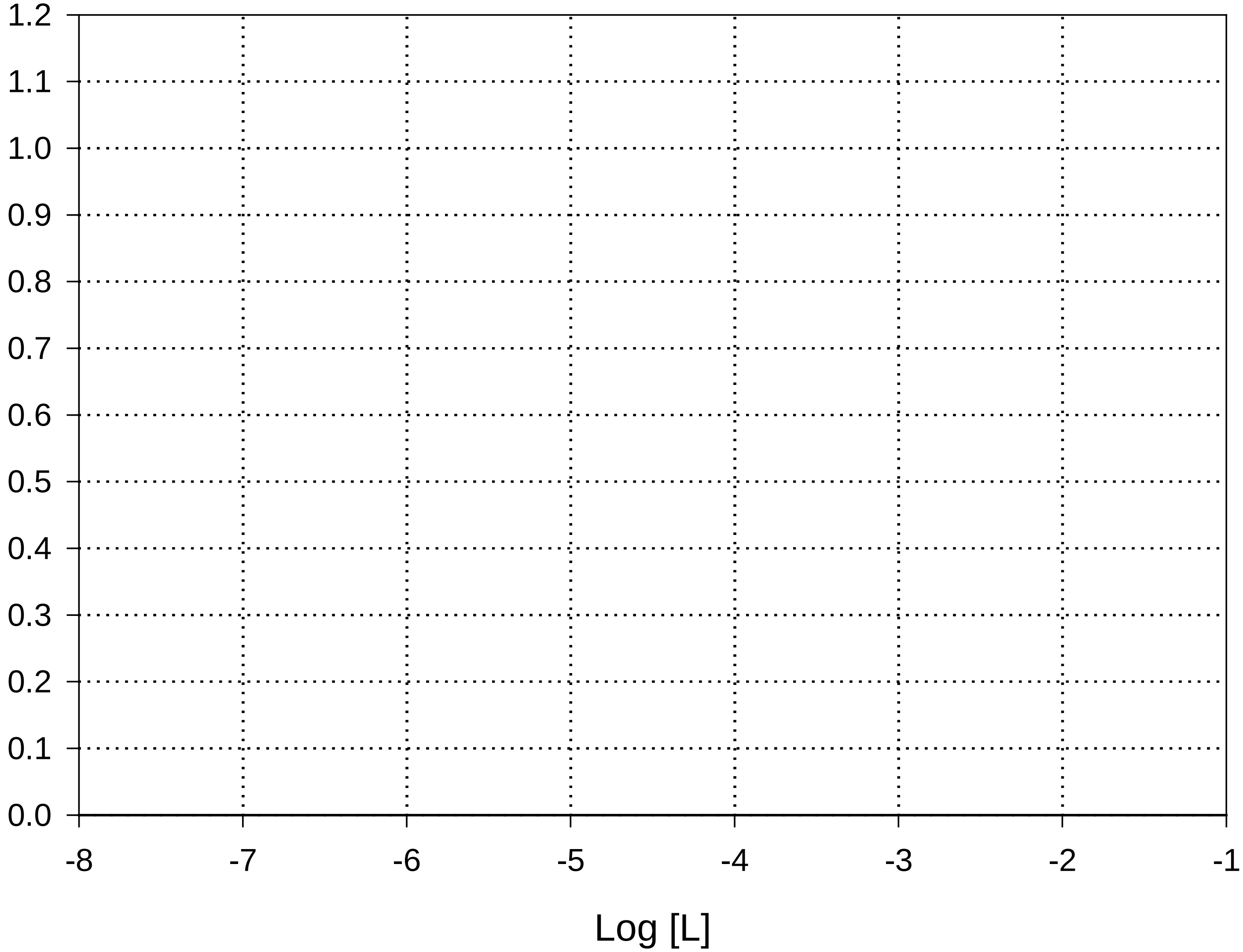
a. How much lime must be added (in moles/liter) to raise the pH to 8.3 after initial mixing?
b. Calculate the ratio of [$FeOH^{+2}$]/[Fe^{+3}] and [$Fe(OH)_2^{+}$]/[Fe^{+3}] in the lake after lime addition (i.e., at pH 8.3)
c. If this lake is allowed to reach equilibrium with the bulk atmosphere, what will its final pH be?

Some additional equilibria

Equilibrium	Constant
$FeOH^{+2} = Fe^{+3} + OH^{-}$	$K_1 = 10^{-11.8}$
$Fe(OH)_2^{+} = FeOH^{+2} + OH^{-}$	$K_2 = 10^{-10.5}$
$Fe(OH)_4^{-} = Fe(OH)_2^{+} + 2OH^{-}$	$K_3 = 10^{-12.1}$
$Fe_2(OH)_2^{+4} = 2Fe^{+3} + 2OH^{-}$	$K_{22} = 10^{-25.05}$

Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

NAME	FORMULA	pK_a
Perchloric acid	$HClO_4 = H^+ + ClO_4^-$	-7 STRONG
Hydrochloric acid	$HCl = H^+ + Cl^-$	-3
Sulfuric acid	$H_2SO_4 = H^+ + HSO_4^-$	-3 (&2) ACIDS
Nitric acid	$HNO_3 = H^+ + NO_3^-$	-0
Hydronium ion	$H_3O^+ = H^+ + H_2O$	0
Trichloroacetic acid	$CCl_3COOH = H^+ + CCl_3COO^-$	0.70
Iodic acid	$HIO_3 = H^+ + IO_3^-$	0.8
Thiocyanic Acid	$HSCN = H^+ + SCN^-$	1.1
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{-2}$	2
Phosphoric acid	$H_3PO_4 = H^+ + H_2PO_4^-$	2.15 (&7.2,12.3)
Citric acid	$C_3H_5O(COOH)_3 = H^+ + C_3H_5O(COOH)_2COO^-$	3.14 (&4.77,6.4)
Hydrofluoric acid	$HF = H^+ + F^-$	3.2
Nitrous acid	$HNO_2 = H^+ + NO_2^-$	4.5
Acetic acid	$CH_3COOH = H^+ + CH_3COO^-$	4.75
Propionic acid	$C_2H_5COOH = H^+ + C_2H_5COO^-$	4.87
Carbonic acid	$H_2CO_3 = H^+ + HCO_3^-$	6.35 (&10.33)
Hydrogen sulfide	$H_2S = H^+ + HS^-$	7.02 (&13.9)
Dihydrogen phosphate	$H_2PO_4^- = H^+ + HPO_4^{-2}$	7.2
Hypochlorous acid	$HOCl = H^+ + OCl^-$	7.5
Boric acid	$B(OH)_3 + H_2O = H^+ + B(OH)_4^-$	9.2 (&12.7,13.8)
Ammonium ion	$NH_4^+ = H^+ + NH_3$	9.24
Hydrocyanic acid	$HCN = H^+ + CN^-$	9.3
Phenol	$C_6H_5OH = H^+ + C_6H_5O^-$	9.9
m-Hydroxybenzoic acid	$C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$	9.92
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{-2}$	10.33
Monohydrogen phosphate	$HPO_4^{-2} = H^+ + PO_4^{-3}$	12.3
Bisulfide ion	$HS^- = H^+ + S^{-2}$	13.9
Water	$H_2O = H^+ + OH^-$	14.00
Methane	$CH_4 = H^+ + CH_3^-$	34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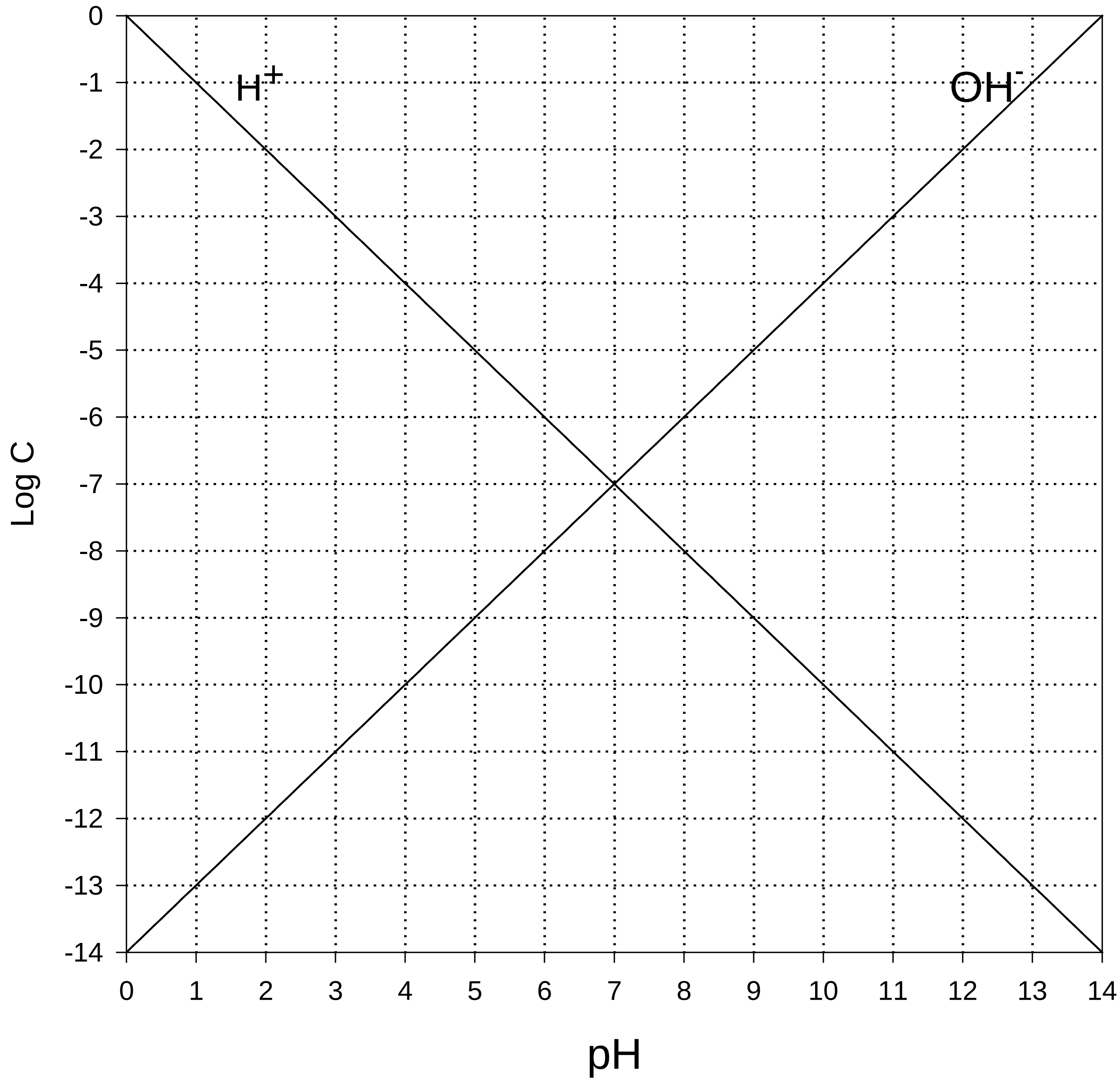
Log [L]



H+
OH-
Log C
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-1
-2
-3
-4
-5
-6
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-8
-9
-10
-11
-12
-13
-14
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
pH