CEE 680 25 April 2019

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	10	6.30
#2	10	350	9.50

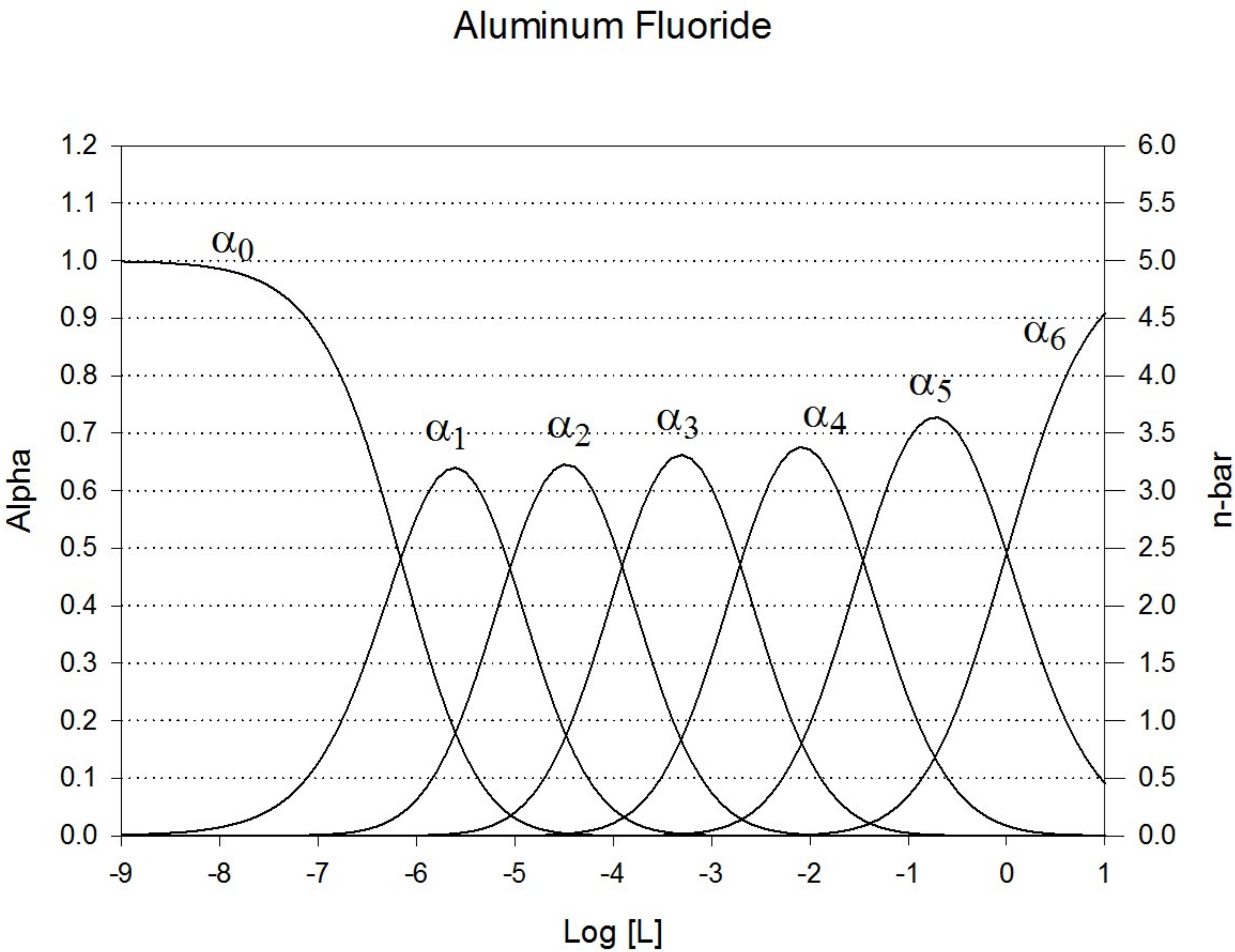
A. What will the pH of the blended water be immediately after mixing?
B. What will the pH of the blended water be after it has reached equilibrium with the bulk atmosphere?
C. How many mg/L of caustic soda (NaOH) must be added to the unequilibrated blended water in part "A" to raise the pH to 9.80 ?

2. Complexation

(50% total for all 4 parts) Fluoride forms few strong complexes. Aluminum 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 Al^{+3} – F^- system. Using this graph determine the complete speciation in an acidified alum solition where the total aluminum concentration is 2 mM and the total fluoride concentration is 10 mM. Assume the pH of the is low enough to render any hydroxide complexes insignificant.
B. (10%) Now explain in qualitative terms how the speciation would change if the alum solution pH was substantially elevated so that hydroxide complexes became important and justify your answer using your knowledge of water chemistry
C. (10%) Explain in qualitative terms how the speciation would change if the pH was high, and if 2 mM of EDTA was added. Note that EDTA does not form precipitates. 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 ideal infinite dilution case (i.e., no ionic strength). Again, justify your answer using your knowledge of water chemistry.


Aluminum Fluoride
Alpha
n-bar
Log [L]
α_0
α_1
α_2
α_3
α_4
α_5
α_6
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1

3. multiple choice

(50%) Answer all 20 of the following questions. The first 10 are multiple choice. Please indicate which of the options is the best choice.

1. Pearson is:
   a. the first name of your textbook's author
   b. the founder of modern environmental chemistry
   c. the originator of a discredited theory
   d. the one who developed the hard and soft acid concept
   e. none of the above

2. When a solution spontaneously absorbs CO_2 from the atmosphere it:
   a. results in higher total carbonate
   b. drops in pH
   c. approaches equilibrium
   d. all of the above
   e. none of the above

3. Phosphate
   a. is a tetradentate ligand
   b. is a deadly poison
   c. is insoluble
   d. is the drug of choice for malaria
   e. has been used as a "builder" in detergents

4. $H_2CO_3^*$:
   a. is composed mostly of aqueous CO_2
   b. is always conservative, even in open systems
   c. is a toxic substance
   d. all of the above
   e. complexes very strongly with sodium

5. Ion pairs:
   a. are always charged
   b. are larger than Bartlett pears
   c. are illegal in Alabama
   d. are outer-sphere complexes

6. The value of n-bar:
   a. is usually 6 or less
   b. depends on the free ligand concentration
   c. can be used to solve complexation problems graphically
   d. all of the above
   e. none of the obove

7. The buffer intensity of the open carbonate system:
  a. is independent of the alkalinity
  b. is independent of the C_T
  c. is always higher than the p_{CO2}
  d. is at a minimum where the pH < pK_1
  e. is at a minimum where the pH = pK_2

8. Detergent “builders” are used to:
  a. help solubilize grease
  b. complex trace metals
  c. take hardness cations from the surfactants
  d. elevate the acidity
  e. reduce the caloric content

9. EDTA
  a. stands for ethylenediamine tetraacetic acid
  b. is most commonly used as a pH buffer
  c. forms precipitates with most metals
  d. is commonly used to enhance the impacts of copper on algae
  e. is a tetra-dentate ligand

10. The Irving Williams Series
  a. is a means of estimating alkalinity
  b. describes the inverse proportionality of acidity to alkalinity
  c. includes a number of books, such as The Chapman Report, and The Prize
  d. provides a comprehensive description of ligand structure
  e. follows the increase in ligand affinity from Mn(II) to Cu(II)

The 10 below are true/false. Mark each one of the following statements with either a “T” or an “F”

11. _____ Mercury forms stronger complexes with iodide than with chloride .

12.______ As metals become more oxidized, they tend to be more prone to hydrolysis

13.______ Most complexation reactions essentially result in complete conversion to products or no conversion at all when at equilibrium

14.______ Phosphate forms stronger complexes than Hydrogen phosphate

15.______ Environmental systems are far more likely to be at equilibrium with respect to precipitation reactions than with respect to acid/base (e.g., proton) equilibrium.

16.______ Oxidation state almost always changes with ligand number.

17.______ The oxidation state of phosphorus in the environment is almost always +V.

18.______ As pH increases, so does the ligand number

19.______ An effective way to keep metals in solution is to add strong ligands like EDTA.

20.______ For the ferrous/ferric systems, oxidation results in stronger complexation.

Additional Information:

For a diprotic acid:

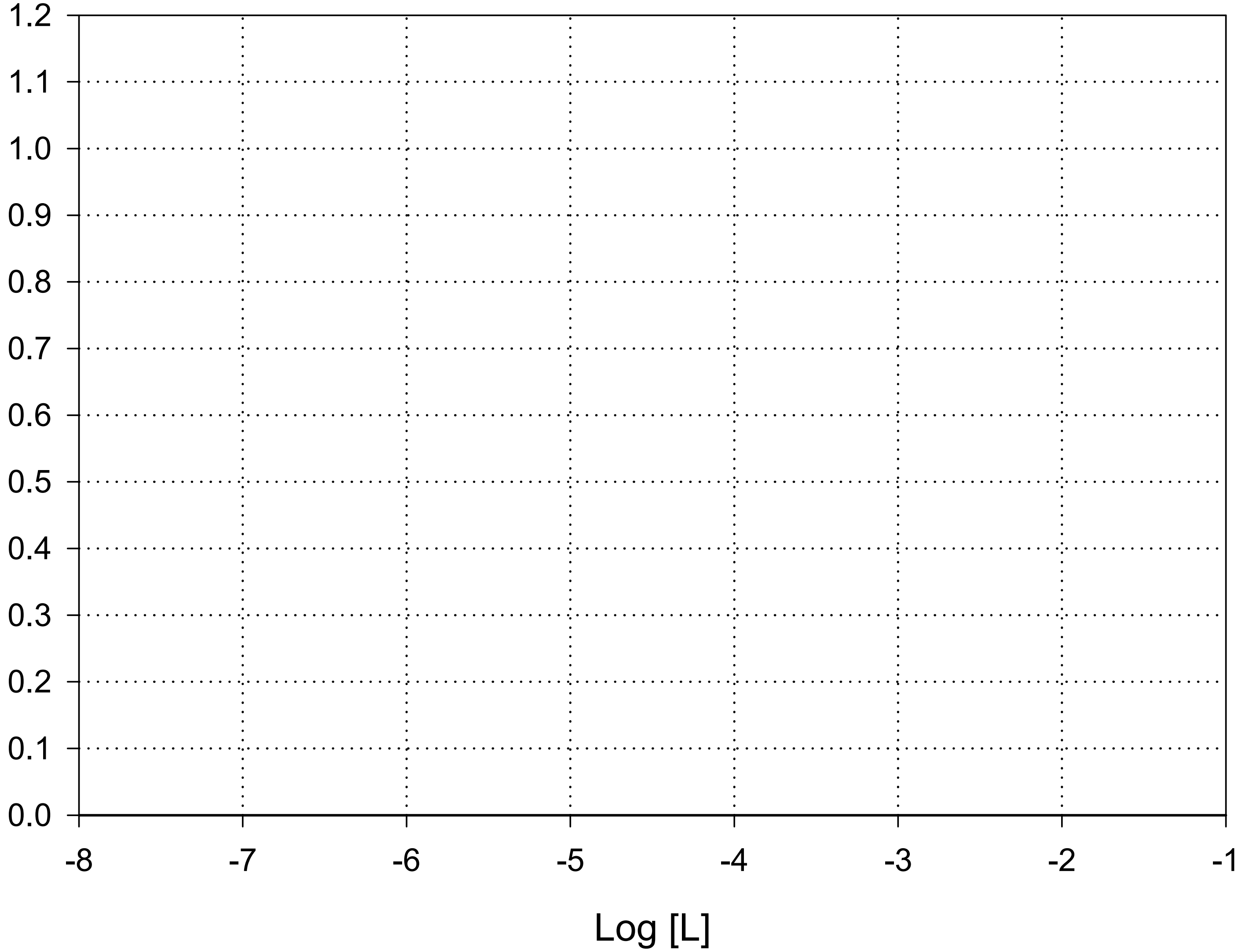
$$\alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}$$

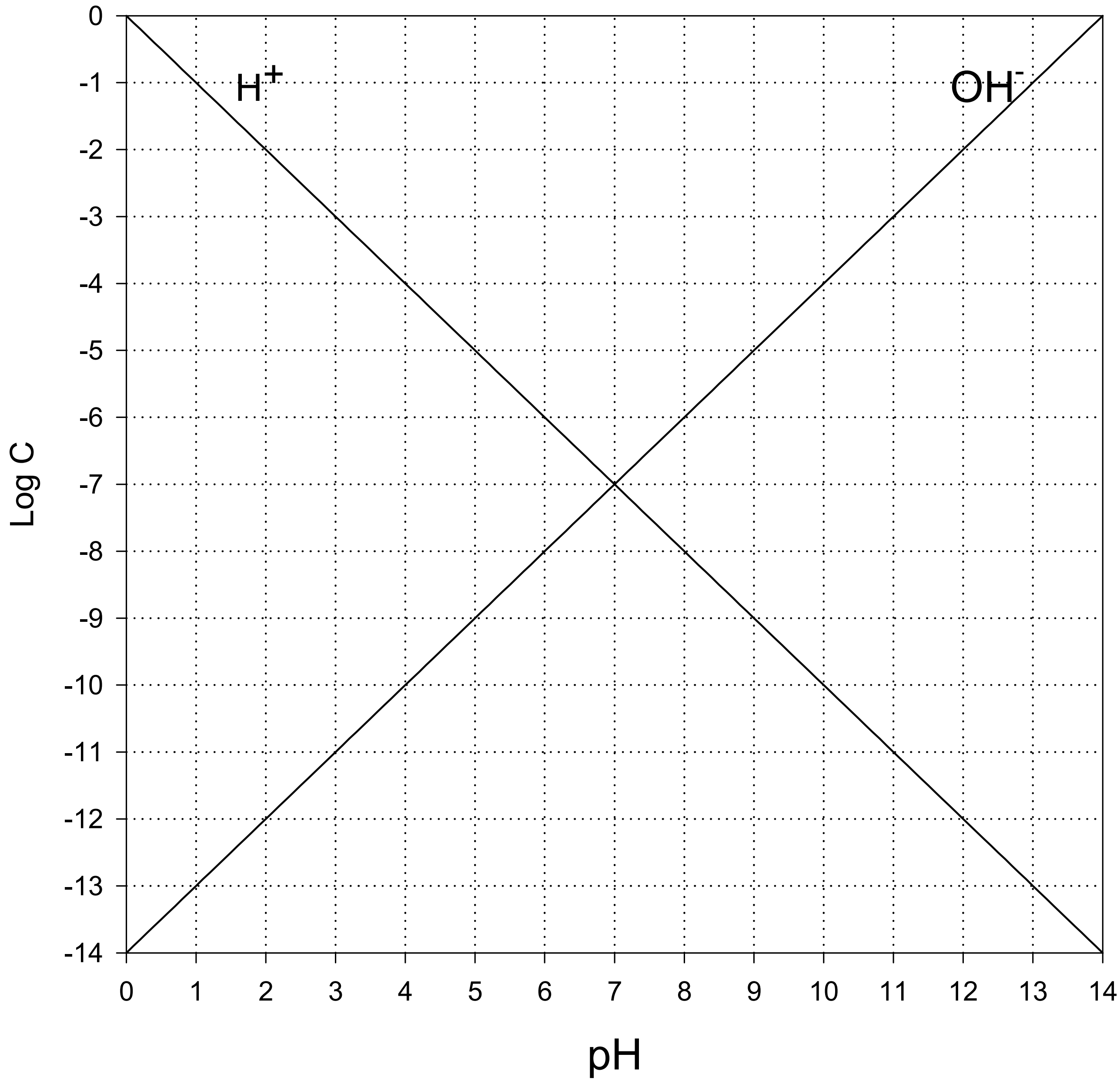
Some additional equilibria

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


1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-8
-7
-6
-5
-4
-3
-2
-1
Log [L]



H+
OH-
Log C
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
pH