CEE 680 20 November 2012

SECOND EXAM

Closed book, two pages of notes allowed.

Answer all 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 1A & B) Two different drinking water supplies are used to provide a total plant flow of 15 MGD. Water #1 is a blended surface water that is held in a large pre-storage basin prior to mixing with Water #2 which is a hard groundwater. The two are characterized as follows:

Water	Flow (MGD)	Alkalinity (mg/L as $CaCO_3$)	pH
#1 prior to equilibration	10	50	7.20
#2	5	250	8.90

A. Determine the Alkalinity, pH and C_T of Water #1 after it has come to equilibrium with the atomosphere in the pre-storage basin.

B. Determine the pH, C_T and alkalinity of the blended water immediately after mixing water #1 with water #2 (remember that water #1 has just been equilibrated with the atmosphere).

2. Complexation

(40% total for both parts) Chloride forms few strong complexes. Mercury is one exception. The following two part problem concerns complexes of this metal-ligand combination.

A. (20%) Below are the equilibria for the Fe^{+2} – HS system as listed in Benjamin's book. Note that are no equilibria for FeL, as this species is never significant. Attached is an accurate graph of alpha values (vs log[HS-]) for the this system. Using this graph determine the complete ferrous-iron speciation in groundwater where the total sulfide concentration is 0.2 mM and total ferrous iron is 0.1 mM. Assume the pH of the groundwater is about 8.

B. (10%) Now explain in qualitative terms how the speciation would change if the groundwater pH was much lower (e.g., pH 5), and much higher (e.g., pH 10) and justify your answers using your knowledge of water chemistry

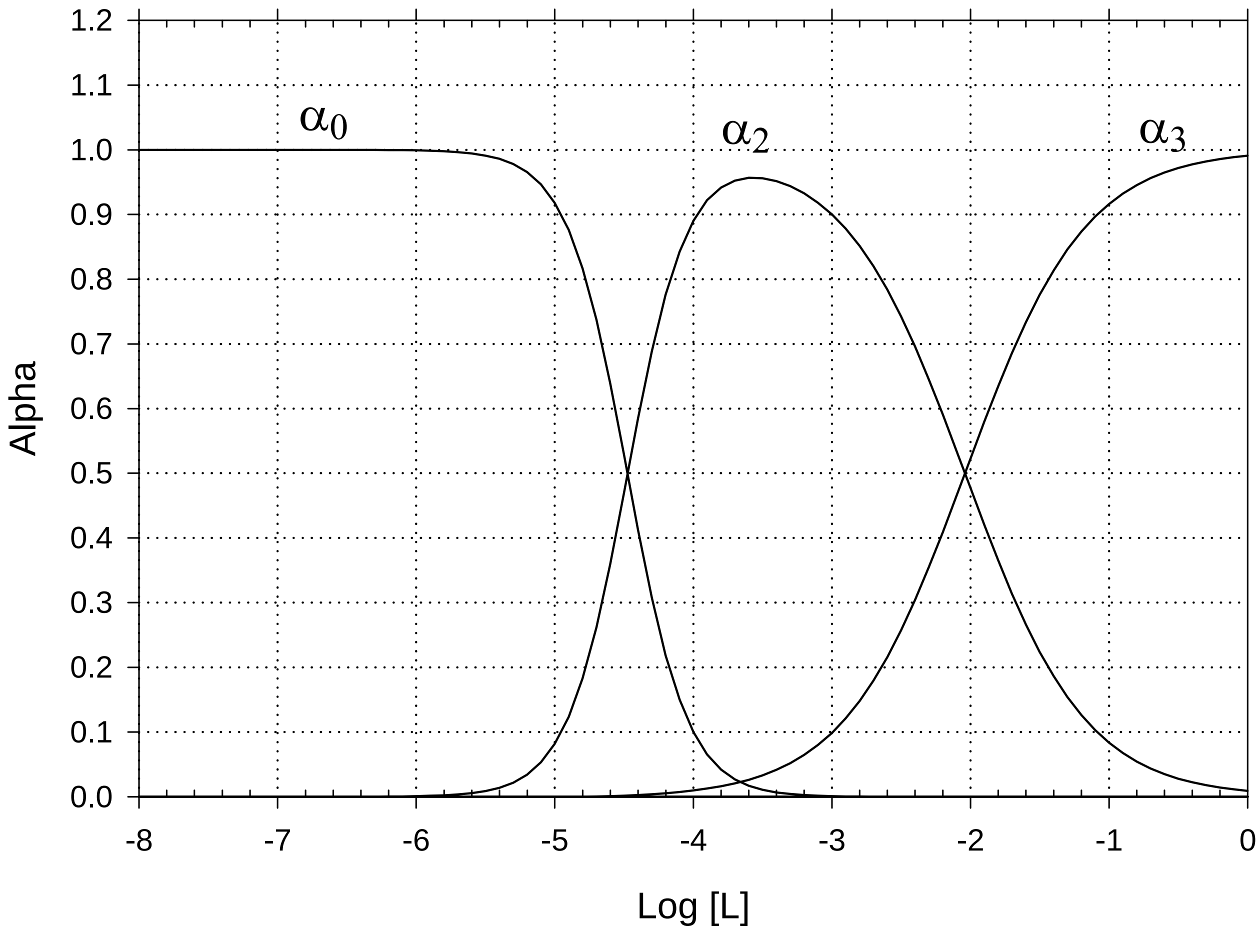
C. (10%) Finally explain in qualitative terms how the speciation would change if the groundwater pH remained at 8, but if carbonate was added and if phosphate was added. Again justify each answer using your knowledge of water chemistry

Log ß values (From Table 8.3 ; pg 374)

Species	Ligand	
	HS-	PO_4^{-3}
FeL_2	8.95	
FeL_3	10.99	
FeH_2L		22.25

Solubility Product Constants (From Table 8.7; pg 398):

Solid	Log K_{so}
$FeCO_3(s)$	-10.55



3. Multiple Choice.

(10%) Answer all 10 of the following questions. Indicate which of the options is the best choice.

1. Hard Acids
   - a. are the only thing that can neutralize hard bases
   - b. prefer ligand atoms of lower atomic weight
   - c. always contain calcium or magnesium
   - d. all of the above
   - e. none of the above

2. Alkalinity is unchanged when:
   - a. carbon dioxide is absorbed from the atmosphere
   - b. sodium nitrate is added
   - c. the system is absorbing oxygen from the atmosphere
   - d. all of the above
   - e. none of the above

3. Surfactants
   - a. are strongly acidic
   - b. do not dissolve in water
   - c. form complexes with hardness cations
   - d. all of the above
   - e. none of the above

4. H_2CO_3*:
   - a. is composed mostly of aqueous CO_2
   - b. is conservative in closed systems
   - c. is an ampholyte
   - d. all of the above
   - e. none of the above

5. A ligand atom:
   - a. is always charged
   - b. forms coordinate covalent bonds with metals
   - c. is almost never dissolved
   - d. only forms outer-sphere complexes
   - e. is usually a metal

6. A bidentate ligand:
   - a. combines with both hard and soft cations
   - b. combines with 2 metals
   - c. always has a minus 2 charge
   - d. is always an organic molecule
   - e. has two ligand atoms

7. The buffer intensity of the acetate/acetic acid system:
   a. is independent of the pH
   b. is independent of the total acetate (C_T)
   c. is zero when the pH is zero.
   d. is at a minimum when the pH is equal to the pH of a pure acetate solution
   e. is at a minimum when the pH = pK

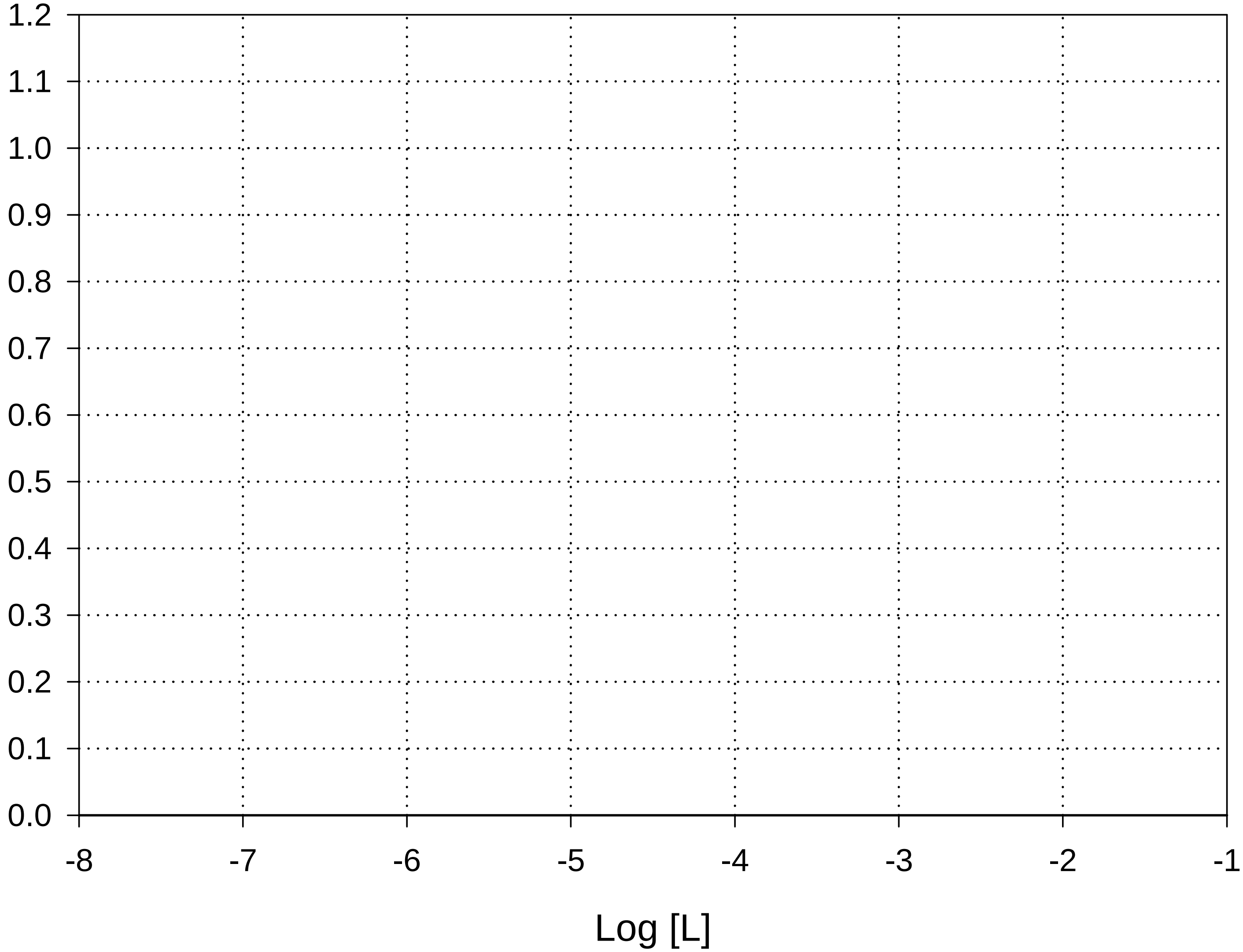
8. Detergent "surfactants" are used to:
   a. help solubilize grease
   b. complex trace metals
   c. take hardness cations from the surfactants
   d. elevate the acidity
   e. reduce the caloric content

9. EDTA
   a. stands for ethylene dioxo-tetraacetic acid
   b. is most commonly used as a pH buffer
   c. is a higly potent carcinogen
   d. all of the above
   e. none of the above

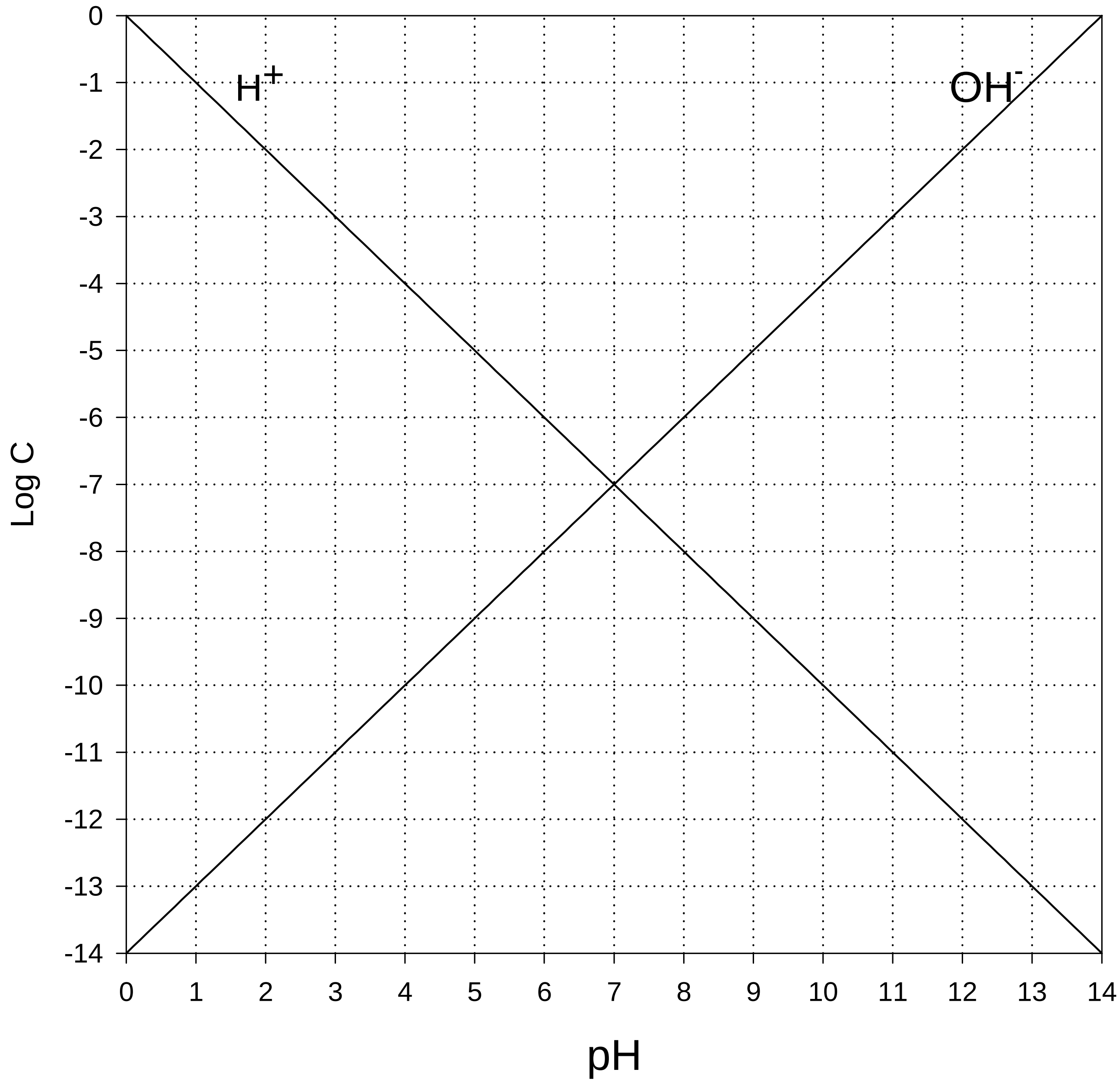
10. As metals become more highly charged, they:
   a. tend to be more strongly bound to most ligands
   b. tend to hydrolyze to a greater extent
   c. they have a greater tendency to form oxo-complexes
   d. all of the above
   e. none of the above

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
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



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