CEE 680 19 November 2013

# 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<br>$K_H = 10^{-1.5}$ M/atm |

## 1. Carbonate System.

(50% for 1A,B & C) 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:

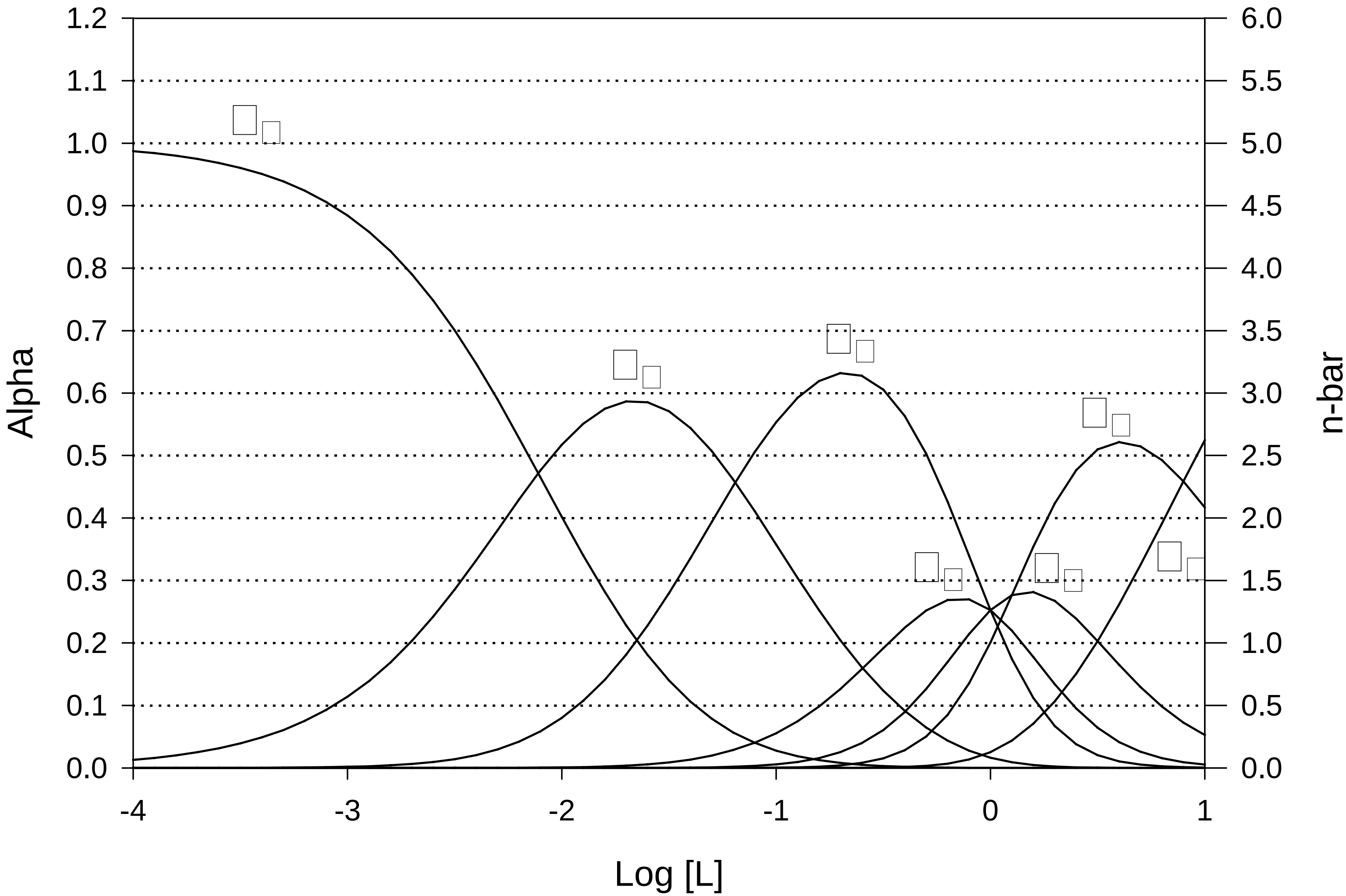
| Water | Flow (MGD) | Alkalinity (mg/L as $CaCO_3$) | pH |
|---|---|---|---|
| #1 prior to equilibration | 10 | 5 | 7.20 |
| #2 | 5 | 250 | 8.90 |

A. Draw an open system diagram for carbonates in equilibrium with the bulk atmosphere
B. Determine the Alkalinity, pH and $C_T$ of Water #1 after it has come to equilibrium with the atomosphere in the pre-storage basin.
C. 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

(50% total for both parts) Thiocyanate (SCN-) will form strong complexes with ferric iron. The following two part problem concerns complexes of this metal-ligand combination.

**A.** (20%) Attached is an accurate graph of alpha values (vs log[SCN-]) for the the Fe-SCN system. Using this graph determine the complete ferric-iron speciation in an industrial wastewater where the total thiocyanide concentration is 0.03 M and total ferric iron is 0.01 M. Note that this is a highly acidic wastewater with a pH of about 1.
**B.** (10%) Now explain how this would change if the total ferric iron was 0.001M. Calcuate the approximate concentrations of all species using this diagram.
**C.** (10%) Next explain in qualitative terms how the speciation would change if the wastewater pH was near neutral (e.g., pH 7) and justify your answers using your knowledge of water chemistry
**D.** (10%) Finally explain in qualitative terms how the speciation would change if the wastewater pH remained at 7, and if phosphate was also present. Again justify each answer using your knowledge of water chemistry



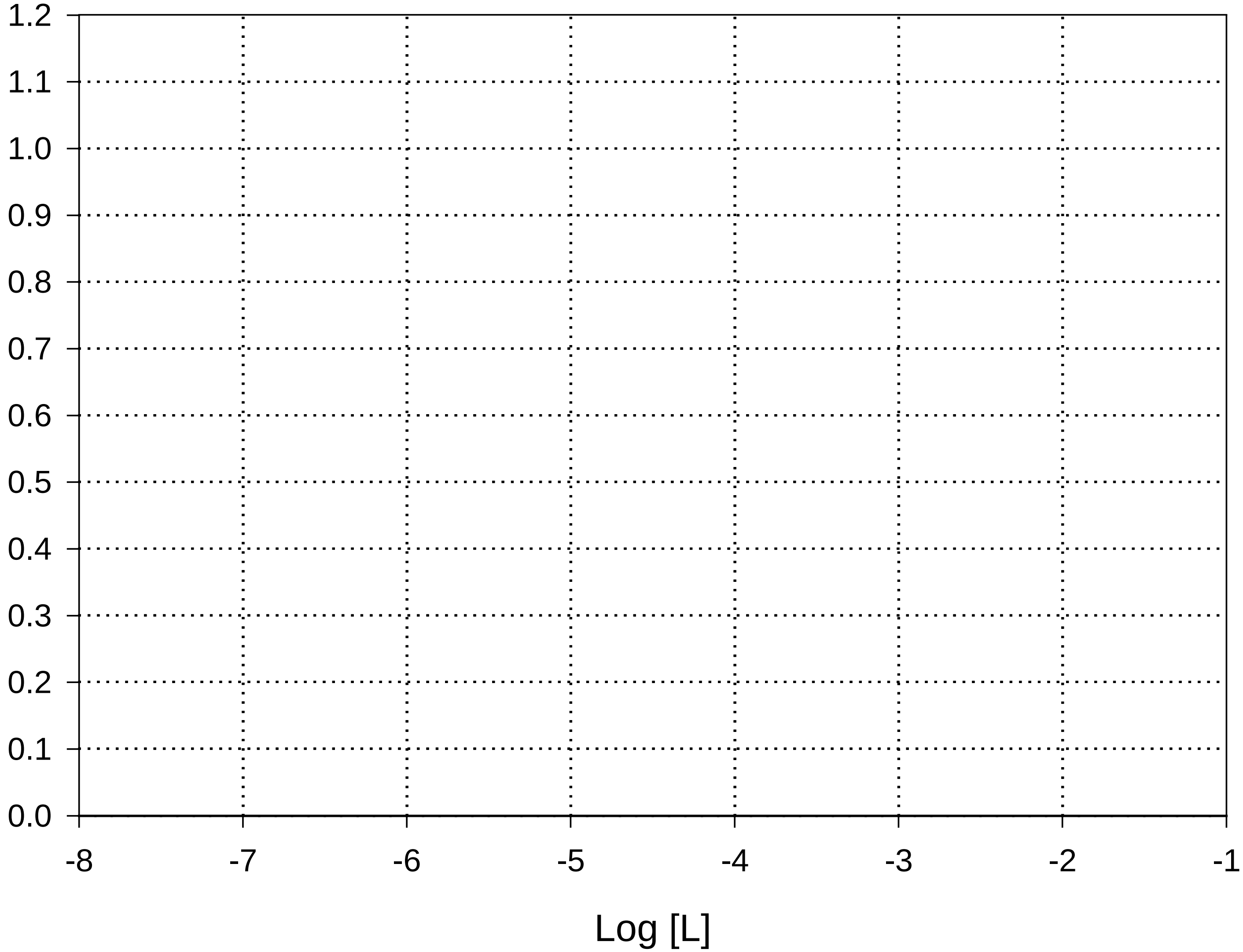
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Alpha
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
n-bar
-4
-3
-2
-1
0
1
Log [L]

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 |

Some additional equilibria

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


1.2
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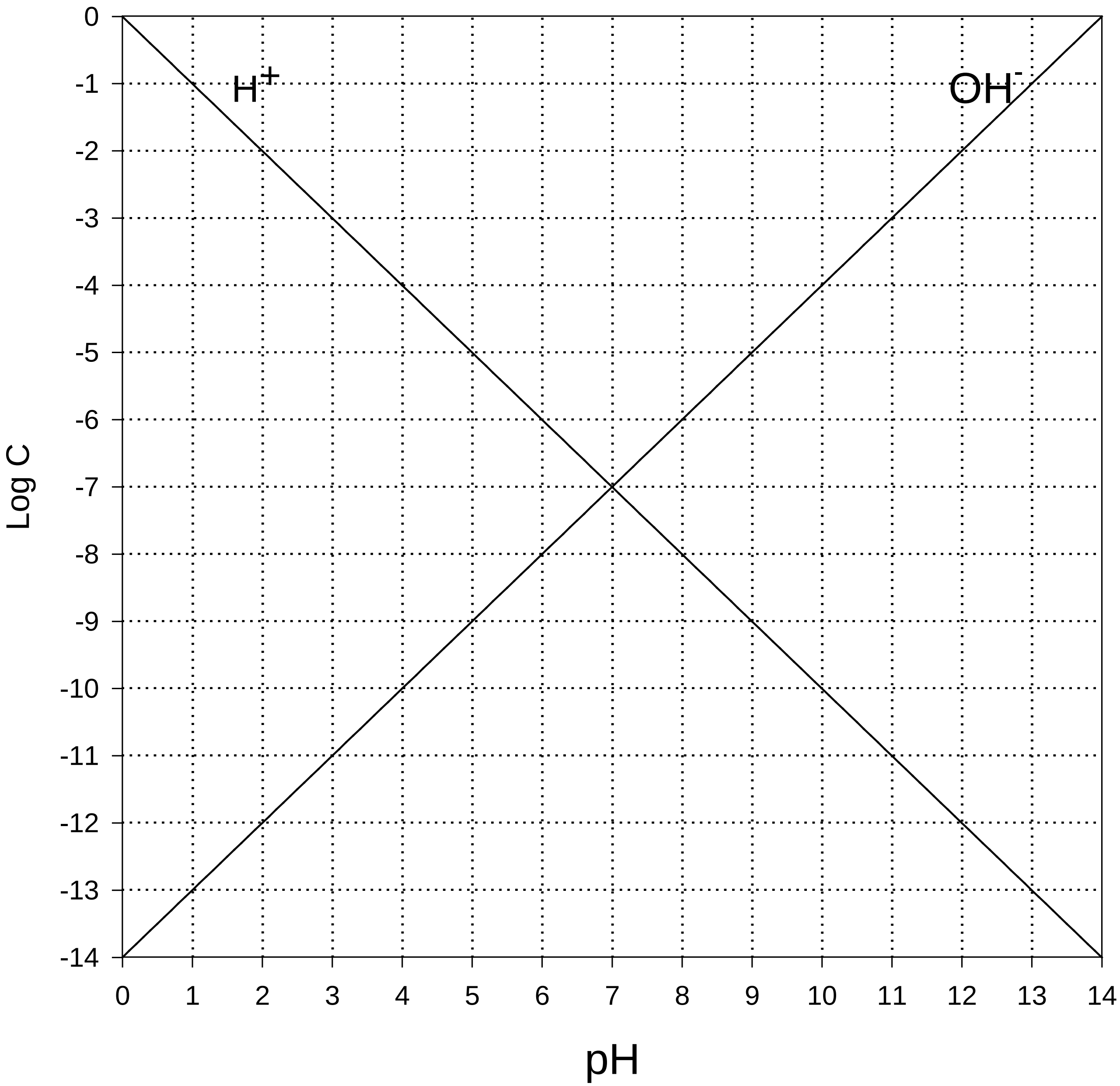
0.5
0.4
0.3
0.2
0.1
0.0
-8
-7
-6
-5
-4
-3
-2
-1
Log [L]



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