CEE 680 22 November 2011

SECOND EXAM

Closed book, two pages of notes allowed.

Answer all questions. Please state any additional assumptions you made, and show all work.

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 badly polluted surface water that has elevated levels of ammonia. Water #2 is a relatively pristine groundwater. The two are characterized as follows:

Water	**Flow (MGD)**	**Alkalinity (mg/L as $CaCO_3$)**	**Ammonia (mg-N/L)**	**pH**
#1	10	5	2	6.50
#2	5	250	~0	8.20

A. Water #1 is pre-treated with sodium hypochlorite[1] to oxidize the ammonia[2] to nitrogen gas prior to blending with water #2. What is the pH of water #1 after sodium hypochlorite (NaOCl) addition. Assume the reaction with chlorine is stoichiometric (see equation below) and assume there are no other reactions occurring.

$$2NH_4^+ + 3NaOCl \rightarrow N_{2(g)} + 2H^+ + 3Na^+ + 3Cl^- + 3H_2O$$

There are several ways to solve this. I based my alkalinity change on the amount of ammonia to be removed, but you could also base it on the requisite chlorine dose

$$\frac{\Delta Alk}{\Delta Ammonia} = \frac{\Delta C_B - \Delta C_A = (3-2)-(3-0)}{2} = -1\frac{eq}{M}$$

The amount of ammonia lost is equal to the amound present in the raw water

Δ Ammonia = 2 mg-N/L = 2/14,000= **<u>0.000143 M</u>**

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[1] Note thas sodium hypochlorite solutions usually come with some NaOH, but for purposes of this problem, let's assume that the solution added is pure NaOCl

[2] Although we call this ammonia, it is really present as ammonium ion (NH_4^+) at all pHs below 9.

Note that a high level of precision is needed to get an accurate pH. For this reason, I will retain many more significant figures than I would normally. And so:

$$\Delta \text{ Alkalinity} = 1 \text{ eq/M} * 0.000143 \text{ M} = \underline{\mathbf{0.000143 \text{ equ}}}$$

And now the final alkalinity is:

$$Alk_f = Alk_i + \Delta Alk = 0.0001 - 0.000143 = -\mathbf{0.000043}\frac{\boldsymbol{equ}}{\boldsymbol{L}}$$

So now we calculate the C_T for this water (which does not change with chlorine addition)

$$C_T = \frac{Alk - [OH^-] + [H^+]}{\alpha_1 + 2\alpha_2}$$

Recall that:

$$\alpha_1 = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{\{H^+]}} \qquad \alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1}$$

and for pH =6.5, we have (using 6.35 and 10.33 as the two pKa's):

$$\underline{\alpha_1 = \mathbf{0.585}} \qquad \underline{\alpha_2 = \mathbf{8.66x10^{-5}}}$$

$$C_T = \frac{0.1x10^{-3} - 10^{-7.5} + 10^{-6.5}}{0.585 + 2(8.66x10^{-5})} = 0.1712x10^{-3}M$$

Now we expect that with a drop in alkalinity, the pH will go well below the first pK,

and the apha's can be simplied for the case where pH<pK$_1$

$$\alpha_1 = \frac{1}{\frac{[H^+]}{K_1}} = \frac{K_1}{[H^+]} \qquad \alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1 K_2}} = \frac{K_1 K_2}{[H^+]^2}$$

$$C_T = \frac{Alk - \left({}^{K_W}/_{\{H^+]}\right) + [H^+]}{\left({}^{K_1}/_{[H^+]}\right) + 2\left({}^{K_1K_2}/_{[H^+]^2}\right)}$$

And if we assume that α_2 will be very small

$$C_T = \frac{Alk - \left({}^{K_W}/_{\{H^+]}\right) + [H^+]}{\left({}^{K_1}/_{[H^+]}\right)}$$

$$C_T = Alk\frac{[H^+]}{K_1} + \frac{K_W}{K_1} + \frac{[H^+]^2}{K_1}$$

$$[H^+]^2 + Alk[H^+] + (K_W - C_TK_1) = 0$$

Solving this with the quadratic formula get us:

pH = 4.351

B. What will the pH of the blended water be immediately after mixing water #1 (remember that this has just been treated with sodium hypochlorite) and water #2?

This is a closed system problem. Therefore the total carbonate concentrations (C_T's) must be determined and treated as conservative. Likewise the alkalinities are conservative, and then the final pH can be determined from the blended C_T and alkalinity.

for either water:

$$C_T = \frac{Alk - [OH^-] + [H^+]}{\alpha_1 + 2\alpha_2}$$

first, I would determine the alpha's at the two pH's. Recall the general equations for a diprotic acid are:

$$\alpha_1 = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}}$$

$$\alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1}$$

This results in the following values (assuming pKs of 6.3 and 10.3:

pH	α_1	α_2
4.351	0.00993	$2.04\text{x}10^{-8}$
8.20	0.97892	0.007257

so, for water #1:

$C_T = \{(-2.14/50{,}000) - (10^{-9.649}) + (10^{-4.351})\}/(0.00993 + 2*2.04\text{x}10^{-8}) = 0.0001711$ M

But we didn't have to calculate this again, as it was already determined in part B

and for water #2:

$C_T = \{(250/50{,}000) - (10^{-5.80}) + (10^{-8.20})\}/(0.97892 + 2*0.007257) = 0.0050315$ M

now we need to calculate the blended alkalinities and total carbonates:

Alk = (10*(-2.14) + 5*250)/15/50,000 = 0.0017912 equ/L

$C_T = (10*0.0001711 + 5*0.0050315)/15 = 0.0016381$ M

Now calculate the pH from the earlier equation for total carbonates, and making any one of the following three sets of simplifying assumptions:

1. **Alk is large compared to [OH] and [H]**

$$C_T = \frac{Alk - [OH^-] + [H^+]}{\alpha_1 + 2\alpha_2}$$

which becomes:

$$C_T \approx \frac{Alk}{\alpha_1 + 2\alpha_2}$$

$$C_T(\alpha_1 + 2\alpha_2) \approx Alk$$

$$C_T\left(\frac{1}{{[H]}/{K_1} + 1 + {K_2}/{[H]}} + \frac{2}{{[H]^2}/{K_1K_2} + {[H]}/{K_2} + 1}\right) \approx Alk$$

$$C_T\left(\frac{K_1[H]}{[H]^2 + K_1[H] + K_1K_2} + \frac{2K_1K_2}{[H]^2 + K_1[H] + K_1K_2}\right) \approx Alk$$

$$\frac{K_1[H] + 2K_1K_2}{[H]^2 + K_1[H] + K_1K_2} \approx \frac{Alk}{C_T}$$

$$C_T K_1[H] + C_T 2K_1K_2 \approx Alk[H]^2 + AlkK_1[H] + AlkK_1K_2$$

$$Alk[H]^2 + (AlkK_1 - C_T K_1)[H] + AlkK_1K_2 - C_T 2K_1K_2 \approx 0$$

Now use the quadratic equation:

$$[H^+] = \frac{-(AlkK_1 - C_T K_1) \pm \sqrt{(AlkK_1 - C_T K_1)^2 - 4Alk(AlkK_1K_2 - C_T 2K_1K_2)}}{2Alk}$$

which is simplified to:

$$[H^+] = \frac{-((Alk - C_T)K_1) \pm \sqrt{((Alk - C_T)K_1)^2 - 4Alk((Alk - 2C_T)K_1K_2)}}{2Alk}$$

and (Alk – C_T) is 0.0017912–0.0016381 = -0.00015311

and (Alk – 2C_T) is 0.0017912–2(0.0016381) = –0.00194443

$$[H^+] = \frac{6.839x10^{-11} \pm \sqrt{\left(6.839x10^{-11}\right)^2 - \left(-2.6617x10^{-22}\right)}}{2 * 0.0016381}$$

$$[H^+] = 4.23367x10^{-8}$$

or

pH = 7.373

2. **$HCO_3^- >> CO_3^{-2}$, pH >> pK_1 and Alk is large compared to [OH] and [H]**

$$C_T = \frac{Alk - [OH^-] + [H^+]}{\alpha_1 + 2\alpha_2}$$

which becomes:

$$C_T \approx \frac{Alk}{\alpha_1}$$

$$C_T(\alpha_1) \approx Alk$$

$$C_T\left(\frac{1}{[H]/K_1 + 1 + K_2/[H]}\right) \approx Alk$$

But if pH>>pK_1, then we can ignore the first terms in the denominator of the alpha quotient. So this equation simplifies to:

$$C_T\left(\frac{1}{1 + K_2/[H]}\right) \approx Alk$$

$$C_T\left(\frac{[H]}{[H] + K_2}\right) \approx Alk$$

$$C_T[H] \approx Alk[H] + AlkK_2$$

$$(Alk - C_T)[H] + AlkK_2 \approx 0$$

Now we can solve directly for H+:

$$[H^+] = \frac{AlkK_2}{Alk - C_T}$$

$$= 4.1751x10^{-9}$$

or

pH = 7.379

or,

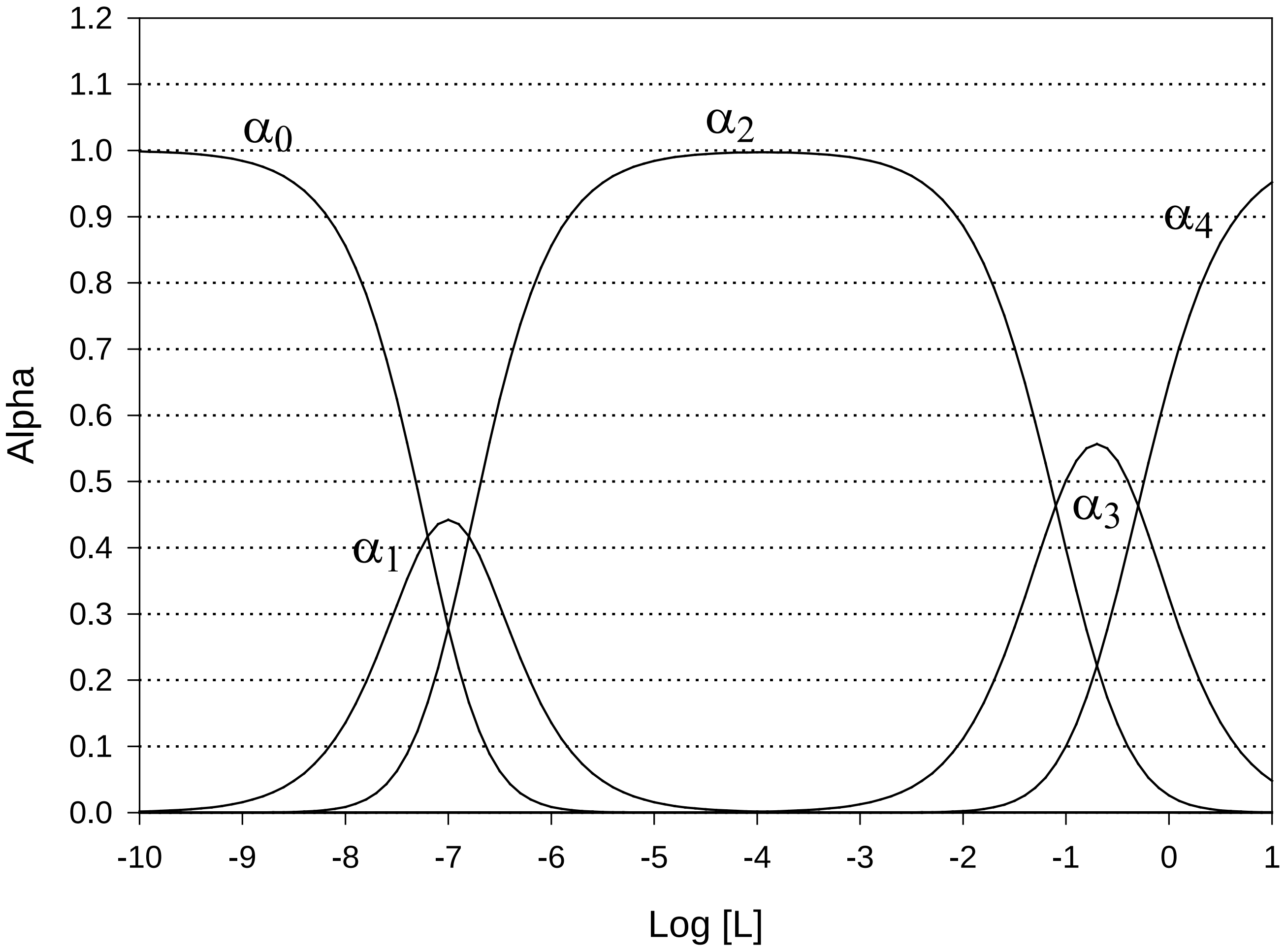
3. **Make no assumptions and solve for the exact solution. This gives:**

pH = 7.3727

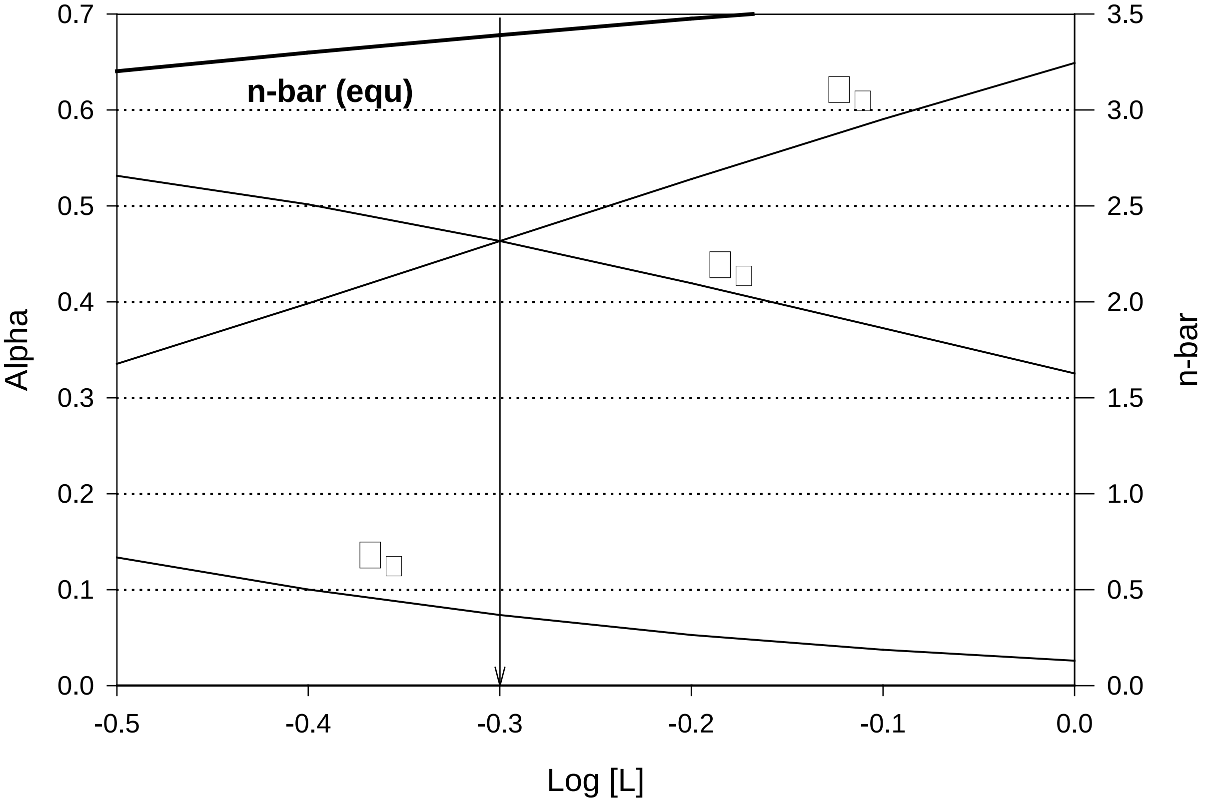
2. Complexation

(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%) Attached is an accurate graph of alpha values (vs log[Cl-]) for the Mercuric Chloride system. Using this graph determine the complete mercury speciation in sea water where free chloride is about 0.5M and total mercury is about 10^{-9}M. Assume the only mercury species are free Hg^{+2} and the various mercuric chloride complexes (i.e., $HgCl_x$).
- **B.** (20%) Now determine the complete compsition of a 10^{-7}M solution of sodium chloride to which you have added 10^{-7} M of $HgCl_2$. Ignore all other mercury complexes except for the chloride ones (i.e., $HgCl_x$).



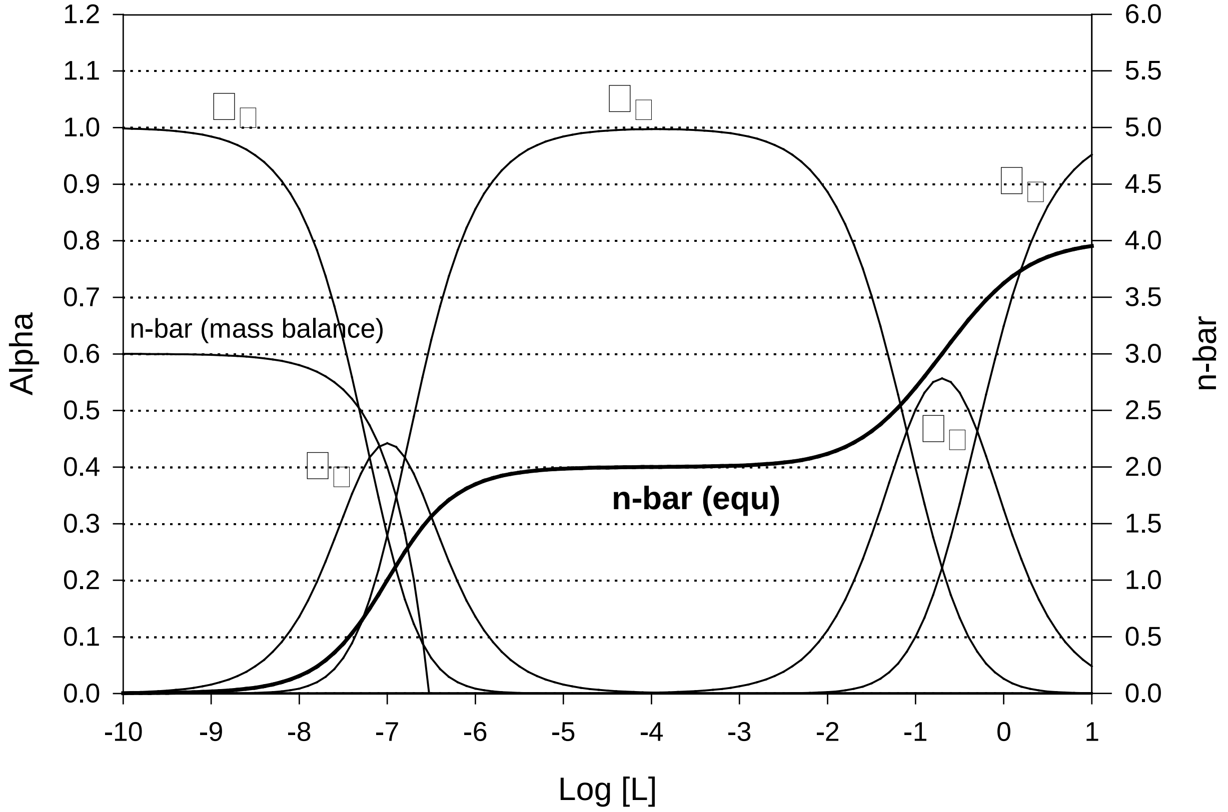
A. Draw a verticle line at L =0.5M or log[L] = -0.30. Then read off the alpha values and determine concentrations. Below is an expanded view of the graph to aide in finding the best values. For the purposes of your exam, you only needed to draw the line over the full sized graph and locate the points as best you can by eye. The correct values are presented in the table below.

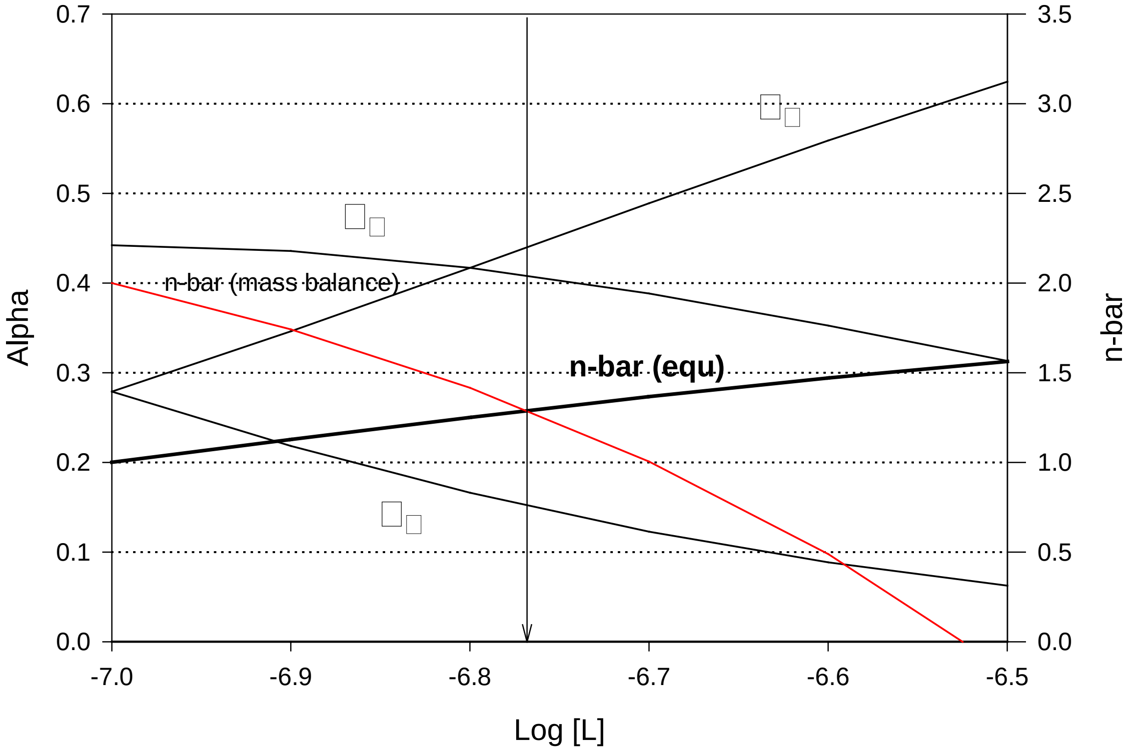


Graph Variable	**Value**	**Species**	**Conc (M)**
L	$10^{-0.30}$	Cl^-	0.5
α_2	0.07	$HgCl_2$	$7x10^{-11}$
α_3	0.465	$HgCl_3^-$	$4.7x10^{-10}$
α_4	0.465	$HgCl_4^{-2}$	$4.7x10^{-10}$

B. Draw the two n-bar lines (equilibrium line and mass balance line). Find the intersection of the two lines and draw a vertical at that point. Then read off the alpha values and determine concentrations. Below is an expanded view of the graph to aide in finding the best values. For the purposes of your exam, you only needed to draw the line over the full sized graph and locate the points as best you can by eye. The correct values are presented in the table below.

$$\overline{n}_{mb} = \frac{C_L - [L]}{C_M} = \frac{3x10^{-7} - [L]}{10^{-7}} = 3 - \frac{[L]}{10^{-7}}$$


Alpha
n-bar
Log [L]
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
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1
n-bar (mass balance)
n-bar (equ)


Alpha
n-bar
Log [L]
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-7.0
-6.9
-6.8
-6.7
-6.6
-6.5
n-bar (mass balance)
n-bar (equ)

Graph Variable	**Value**	**Species**	**Conc (M)**
L	$10^{-6.77}$	Cl^-	$1.7x10^{-7}$
α_0	0.15	Hg^{+2}	$1.5x10^{-8}$
α_1	0.405	$HgCl^+$	$4.0x10^{-8}$
α_2	0.445	$HgCl_2$	$4.5x10^{-8}$

3. Multiple Choice.

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

Question #6 was a bit ambiguous, so I didn't consider this one in the grade

1. The sum of total acidity and total organic carbon on any given sample is equal to
    a. the UV absorbance
    b. twice the total carbonate
    c. the value one
    d. half of the hardness
    e. none of the above

2. Alkalinity is said to be conservative when:
    a. the system being studied is open to the atmosphere
    b. the system being studied is isolated in the subsurface
    c. the system being studied is at alkaline pHs
    d. all of the above
    e. none of the above

3. Phenolphthalein
    a. is a hexadentate ligand
    b. is rarely used because noone can spell it
    c. complexes calcium forming an insoluble salt
    d. is the drug of choice for malaria
    e. changes from colorless to red as pH increases

4. H_2CO_3*:
    a. is composed mostly of aqueous CO_2
    b. is conservative in closed systems
    c. is am 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. none of the above

6. The ligand number:
    a. is usually 6 or less
    b. is related to the molecular weight of the central atom
    c. is a function of the size of the ligand
    d. all of the above
    e. none of the obove

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

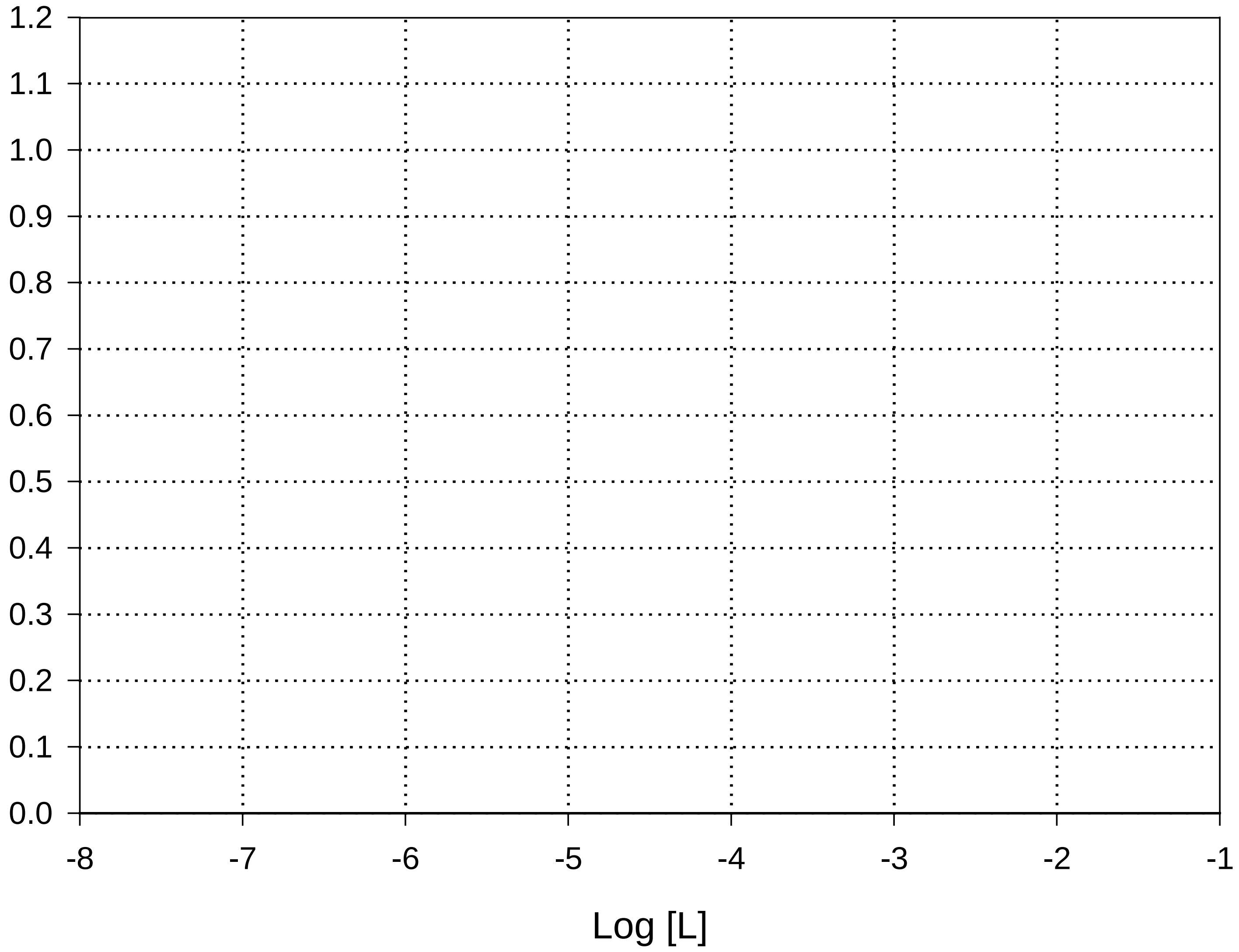
8. Detergent "surfactants" are used to:
    a. help solubilize grease
    b. complex trace metals
    c. take hardness cations from the surfactants
    d. elevate the acidity
    e. reduce the caloric content

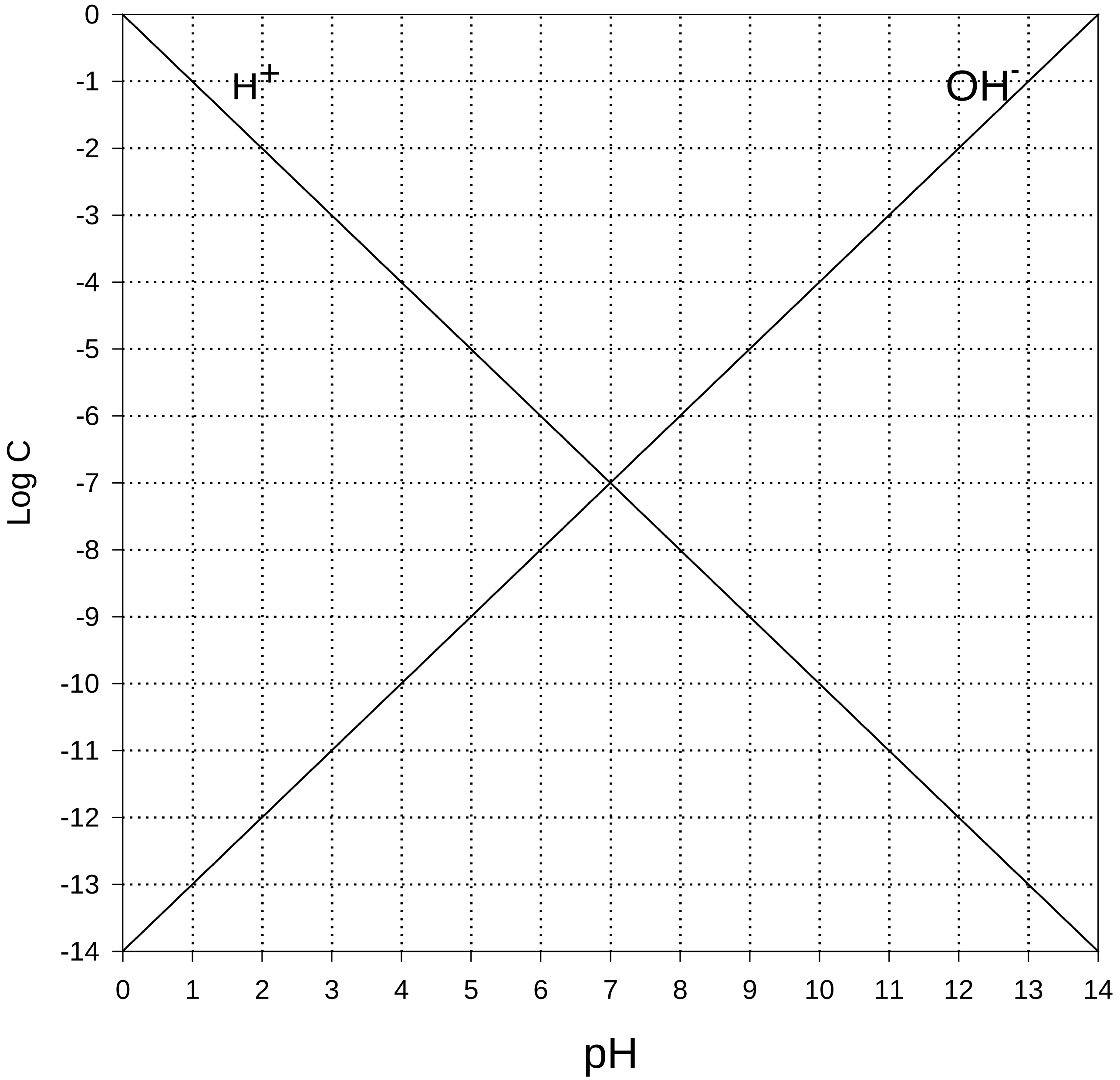
9. EDTA
    a. stands for ethylene dioxo-tetraacetic acid
    b. is most commonly used as a pH buffer
    c. is a higly potent carcinogen
    d. all of the above
    e. none of the above

10. 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. follows the increase in ligand affinity from Mn(II) to Cu(II)
    e. provides a comprehensive description of ligand structure

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