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.

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

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?

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., $HgCl_x$).

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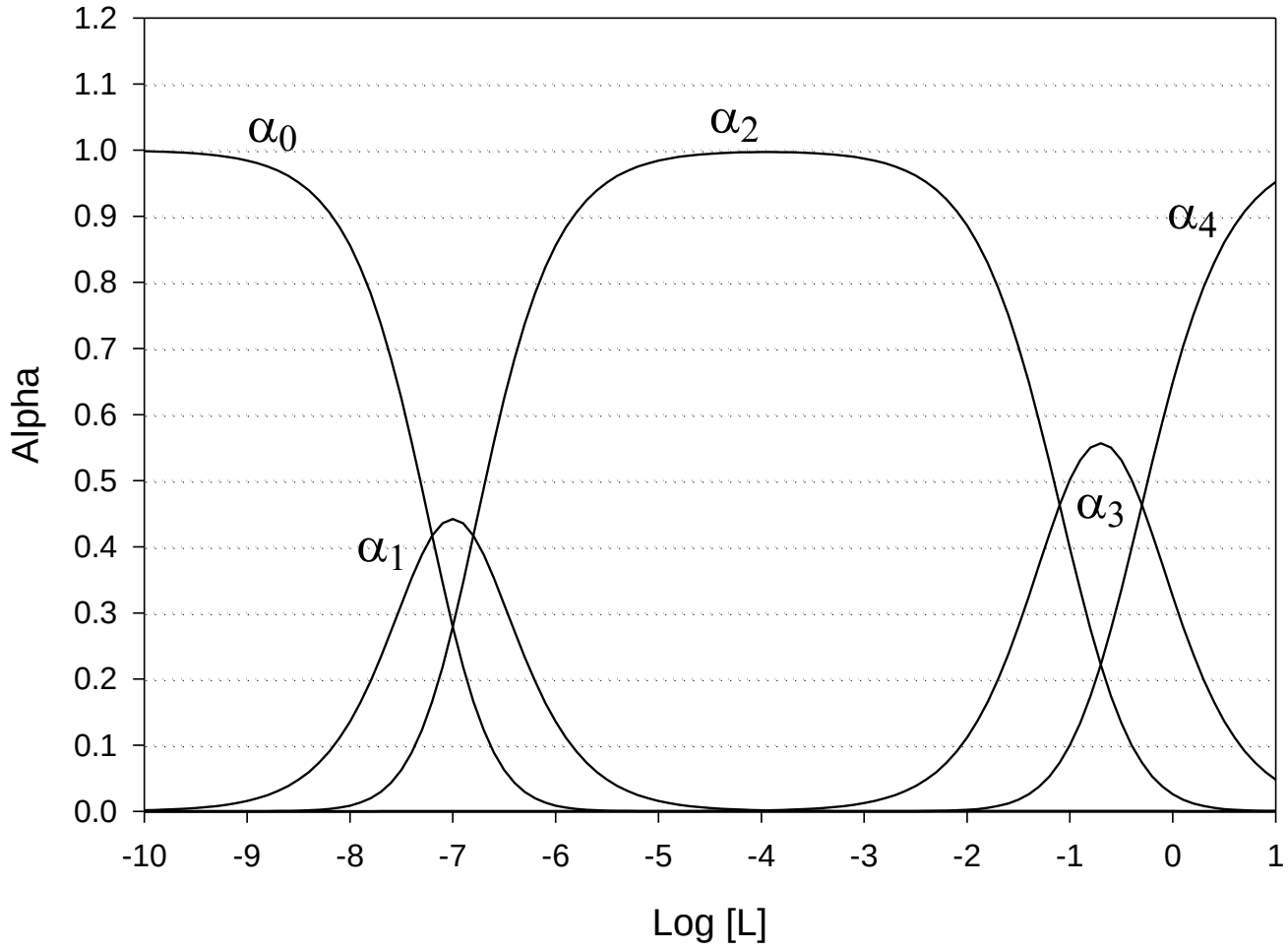
[1] Note thas sodium hypochlorite solutions usually come with some NaOH, but for purposes of this problem, let's assume that the solution added is pure NaOCl

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

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., $HgCl_x$).



3. Multiple Choice.

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

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 fo 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

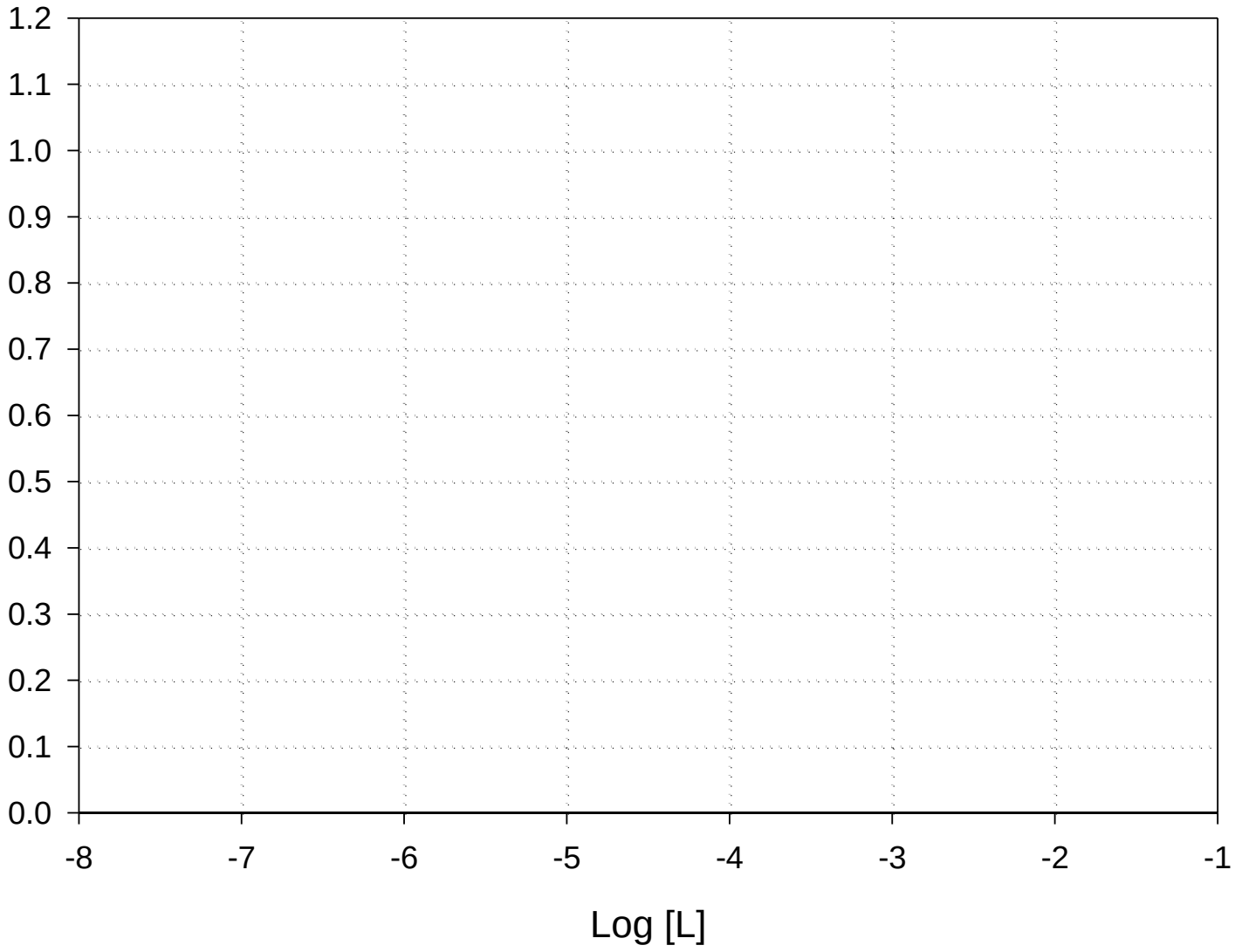
8. Detergent “surfactants” are used to:
    a. help solubilize grease
    b. complex trace metals
    c. take hardness cations from the surfactants
    d. elevate the acidity
    e. reduce the caloric content

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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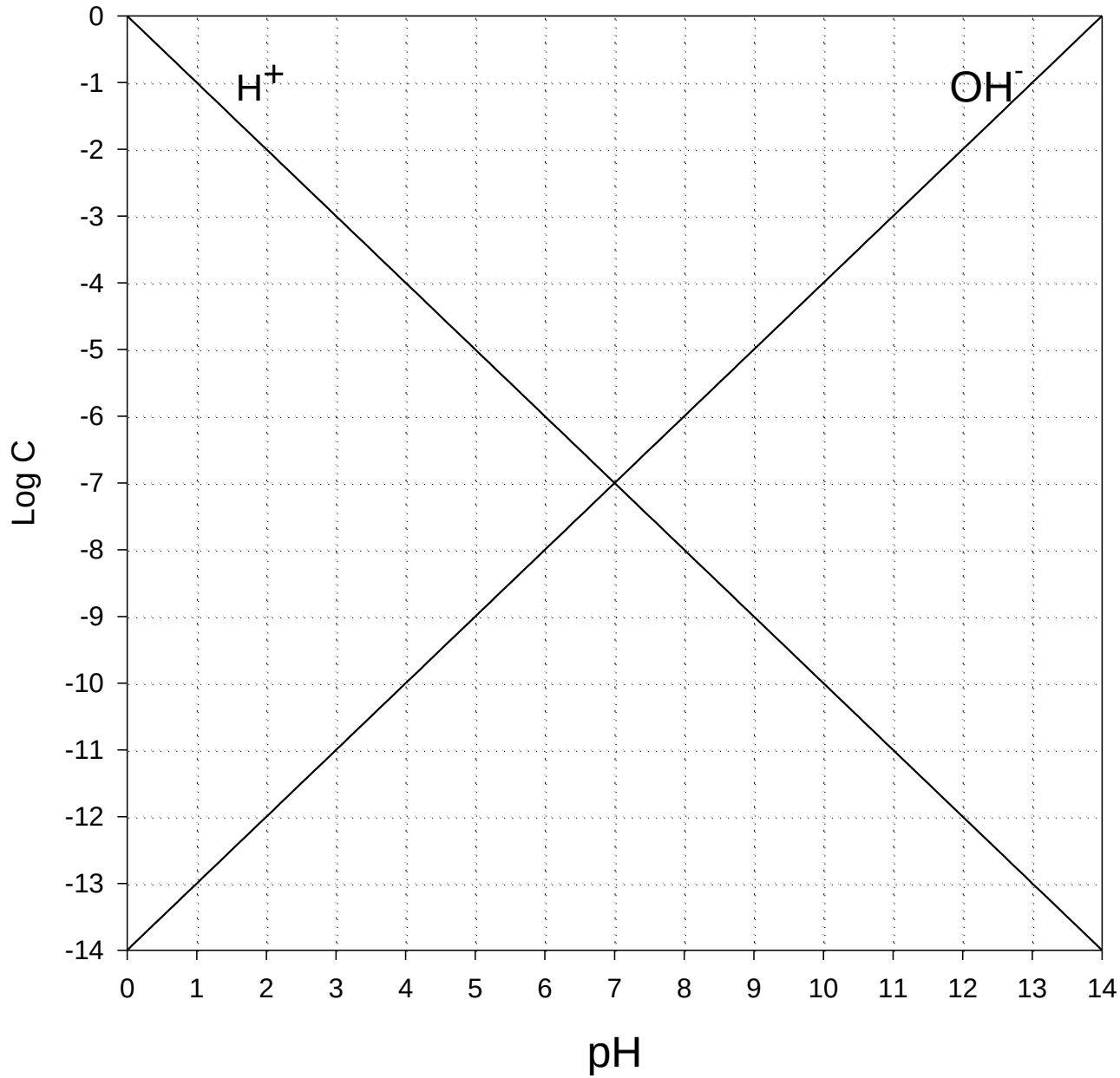
Log [L]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