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<br>$K_H = 10^{-1.5}$ 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).

**Solution to A**

This is now an open system problem.

There are many ways to solve this, depending on the extent of simplifying assumptions you're willing to try. Here are a few examples:

1. **Assume that $H^+$ and $OH^-$ are insignificant**

$$Alk \approx \left([HCO_3^-] + 2[CO_3^{-2}]\right)C_T = \frac{50}{50,000} = 10^{-3}$$

Since this is an open system, we know what $C_T$ is:

$$Alk \approx (\alpha_1 + 2\alpha_2)\left(\frac{K_h p_{CO2}}{\alpha_0}\right)$$

And now:

$$\frac{Alk}{K_h p_{CO2}} \approx \left(\frac{\alpha_1}{\alpha_0} + 2\frac{\alpha_2}{\alpha_0}\right)$$

$$\frac{Alk}{K_h p_{CO2}} \approx \frac{[HCO_3^-]}{[H_2CO_3]} + 2\frac{[CO_3^{-2}]}{[H_2CO_3]}$$

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

$$[H^+]^2 - \frac{K_1K_h p_{CO2}}{Alk}[H^+] - 2\frac{K_1K_2K_h p_{CO2}}{Alk} = 0$$

$$[H^+] = \frac{-\left(\frac{K_1K_h p_{CO2}}{Alk}\right) \pm \sqrt{\left(\frac{K_1K_h p_{CO2}}{Alk}\right)^2 - 4\left(2\frac{K_1K_2K_h p_{CO2}}{Alk}\right)}}{2}$$

$$= 4.559x10^{-9}$$

or

**pH = 8.341**

**2. Assume that bicarbonate is the only carbonate species of any importance.**

Charge balance considerations dictate that:

$Alk = C_T$

Under conditions where $pK_1 << pH << pK_2$, the following is approximately true:

$C_T = [HCO_3^-]$

And from the equilibrium equation we can conclude:

$[HCO_3^-] = K_1 [H_2CO_3^*]/[H^+]$

And since this is an open system, we can say:

$[H_2CO_3^*] = K_H p_{CO2}$

which becomes, for the bulk atmosphere at 25°C

$[H_2CO_3^*] = 10^{-5}$

we can combine and get the equation for alkalinity (or bicarbonate) vs $H^+$ in an open system

$$Alk = [HCO_3^-] = K_1\, 10^{-5} / [H^+]$$

Then substituting and isolating $H^+$, we get

$$[H^+] = 10^{-11.35}/Alk$$

and substituting in for the blended water alkalinity

$$[H^+] = 10^{-11.35}/0.001$$
$$[H^+] = 4.47 \times 10^{-9}$$

or

**pH = 8.35**

**Solution to B**

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 | $\alpha_1$ | $\alpha_2$ |
|---|---|---|
| 8.341 | 0.9799 | 0.01005 |
| 8.90 | 0.9616 | 0.03573 |

so, for water #1:

$C_T$ = {(-2.14/50,000) - ($10^{-9.649}$) + ($10^{-4.351}$)}/(0.9799 + 2*0.01005) = 0.0009978 M

and for water #2:

$C_T$ = {(250/50,000) - ($10^{-5.80}$) + ($10^{-8.20}$)}/(0.9616 + 2*0.03573) = 0.0048325 M

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

Alk = (10*50 + 5*250)/15/50,000 = 0.002333 equ/L

$C_T$ = (10*0.0009978 + 5*0.0048325)/15 = 0.002276 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:

$$[H^+] = \frac{-\left(AlkK_1 - C_T K_1\right) \pm \sqrt{\left(AlkK_1 - C_T K_1\right)^2 - 4Alk\left(AlkK_1 K_2 - C_T 2K_1 K_2\right)}}{2Alk}$$

which is simplified to:

$$[H^+] = \frac{-\left((Alk - C_T)K_1\right) \pm \sqrt{\left((Alk - C_T)K_1\right)^2 - 4Alk\left((Alk - 2C_T)K_1 K_2\right)}}{2Alk}$$

and (Alk – $C_T$) is 0.002333–0.002276 = -0.0000573

and (Alk – 2$C_T$) is 0.002333–2(0.002276) = –0.002219

$$[H^+] = \frac{2.56x10^{-11} \pm \sqrt{\left(2.56x10^{-11}\right)^2 - \left(-4.3265x10^{-22}\right)}}{2 * 0.0023333}$$

$$[H^+] = 1.52x10^{-9}$$

or

**pH = 8.801**

2. **$HCO_3^-$>> $CO_3^{-2}$, pH >> p$K_1$ 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+:

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

$$=1.81x10^{-9}$$

or

**pH = 8.742**

or,

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

**pH = 8.7644**

## 2. Complexation

(40% total for both parts) The following two part problem concerns complexes of the ferrous-bisulfide 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

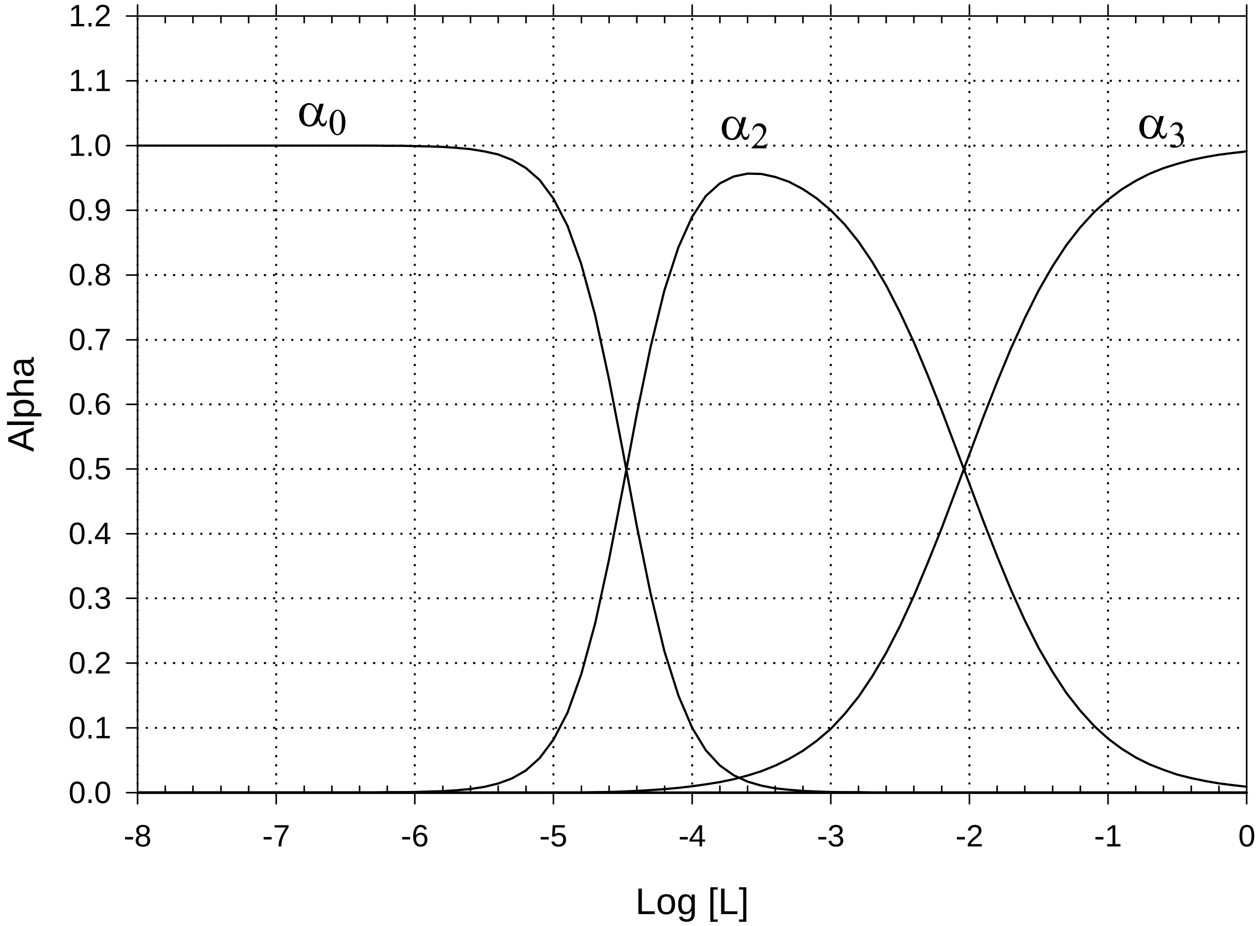
**C.** (10%) Finally explain in qualitative terms how the speciation would change if the groundwater pH remained at 8, but if carbonate was added and if phosphate was added. Again justify each answer using your knowledge of water chemistry

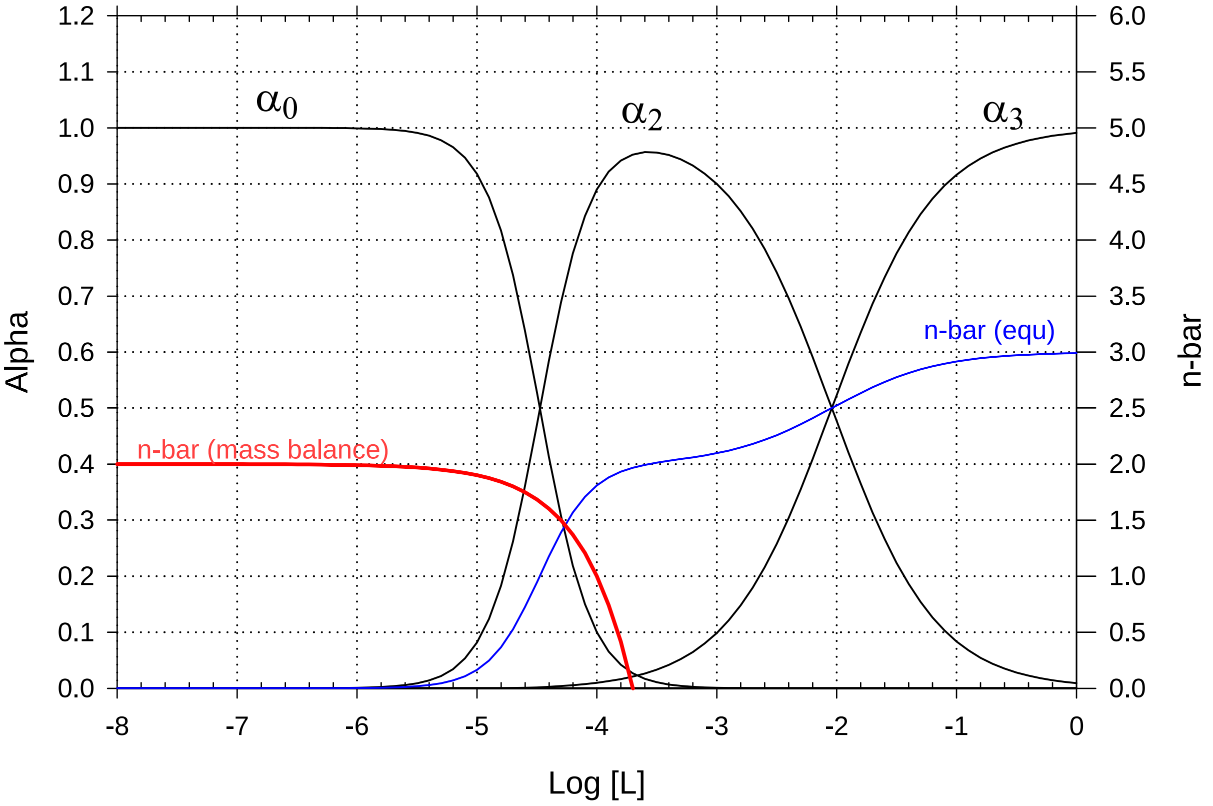
Log ß values (From Table 8.3 ; pg 374)

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

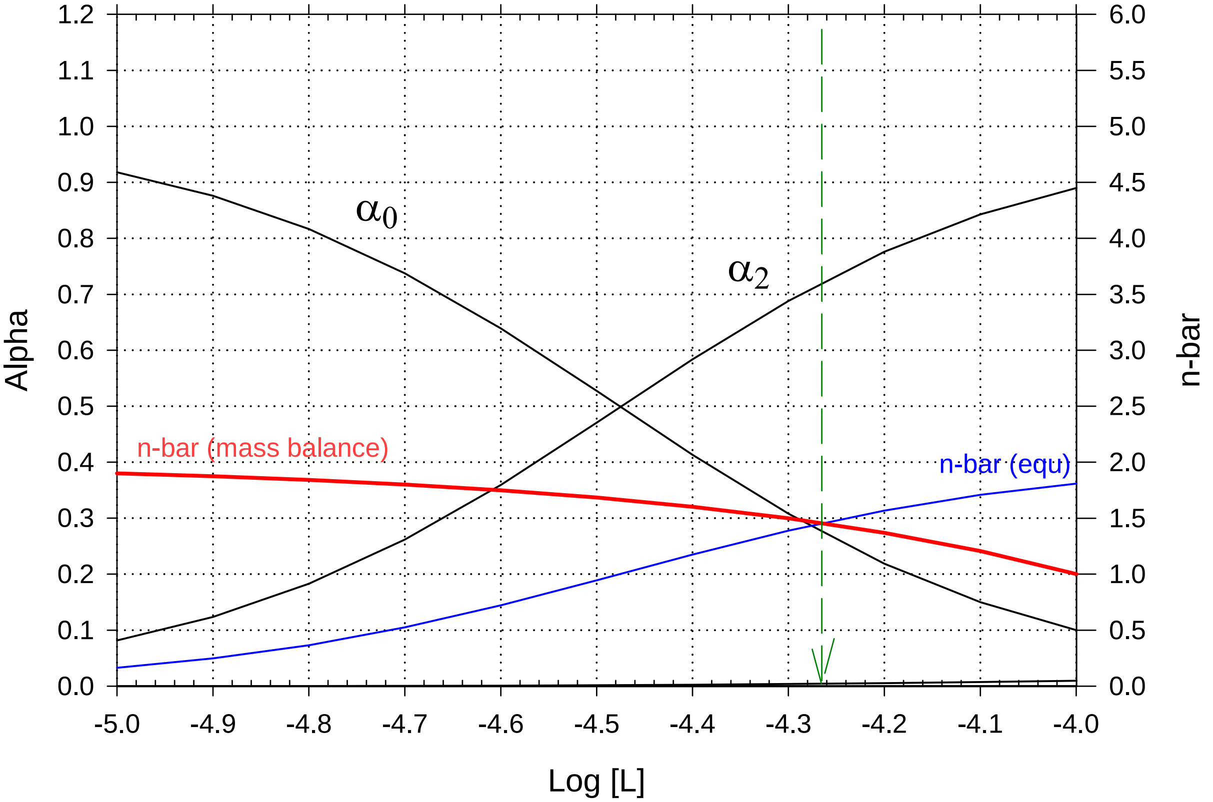
Solubility Product Constants (From Table 8.7; pg 398):

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





Alpha
n-bar
Log [L]
$\alpha_0$
$\alpha_2$
$\alpha_3$
n-bar (equ)
n-bar (mass balance)
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
-8
-7
-6
-5
-4
-3
-2
-1
0



Alpha
n-bar
Log [L]
$\alpha_0$
$\alpha_2$
n-bar (mass balance)
n-bar (equ)
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
-5.0
-4.9
-4.8
-4.7
-4.6
-4.5
-4.4
-4.3
-4.2
-4.1
-4.0

Intersection occurs at about Log [L] = -4.27.
Alpha values are about: 0.27, 0.73, and 0, respectively.

| Species | Conc (M) | Log C |
|---|---:|---:|
| HS- | **5.37E-05** | **-4.27** |
| $Fe^{+2}$ | **2.70E-05** | **-4.57** |
| $Fe(HS)_2^o$ | **7.30E-05** | **-4.14** |
| $Fe(HS)_3^-$ | **0** | |
| $H^+$ | **1.00E-08** | **-8** |
| $OH^-$ | **1.00E-06** | **-6** |
| $H_2S$ | **5.75E-06** | **-5.24** |
| $S^{-2}$ | **5.37E-11** | **-10.27** |

Note that:

$$\frac{[H_2S]}{[HS]} = \frac{[H^+]}{K_1}$$

$$\frac{[S^{-2}]}{[HS]} = \frac{K_2}{[H^+]}$$

B. Lower pH would result in a shift of HS- to $H_2S$, effectively reducing the available “L” and less complexation A higher pH would shift it to $S^{-2}$ and possible do the same. Mitigating factors would be the possible existence of FeS complexes. On the other had higher pHs would result in OH complexes of Fe and possibly precipitation of Ferrous hydroxide

C. Carbonate would result in precipitation of Ferrous Carbonate (note Kso value) and therefore higher n-bar values based on mass balance. This would mean lower soluble iron, but higher degrees of complexation of the iron that is present. On the other had phosphate might only form additional complexes and compete with the HS for iron. This would result in increases in the soluble iron, and smaller amounts of free aquo iron.

## 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

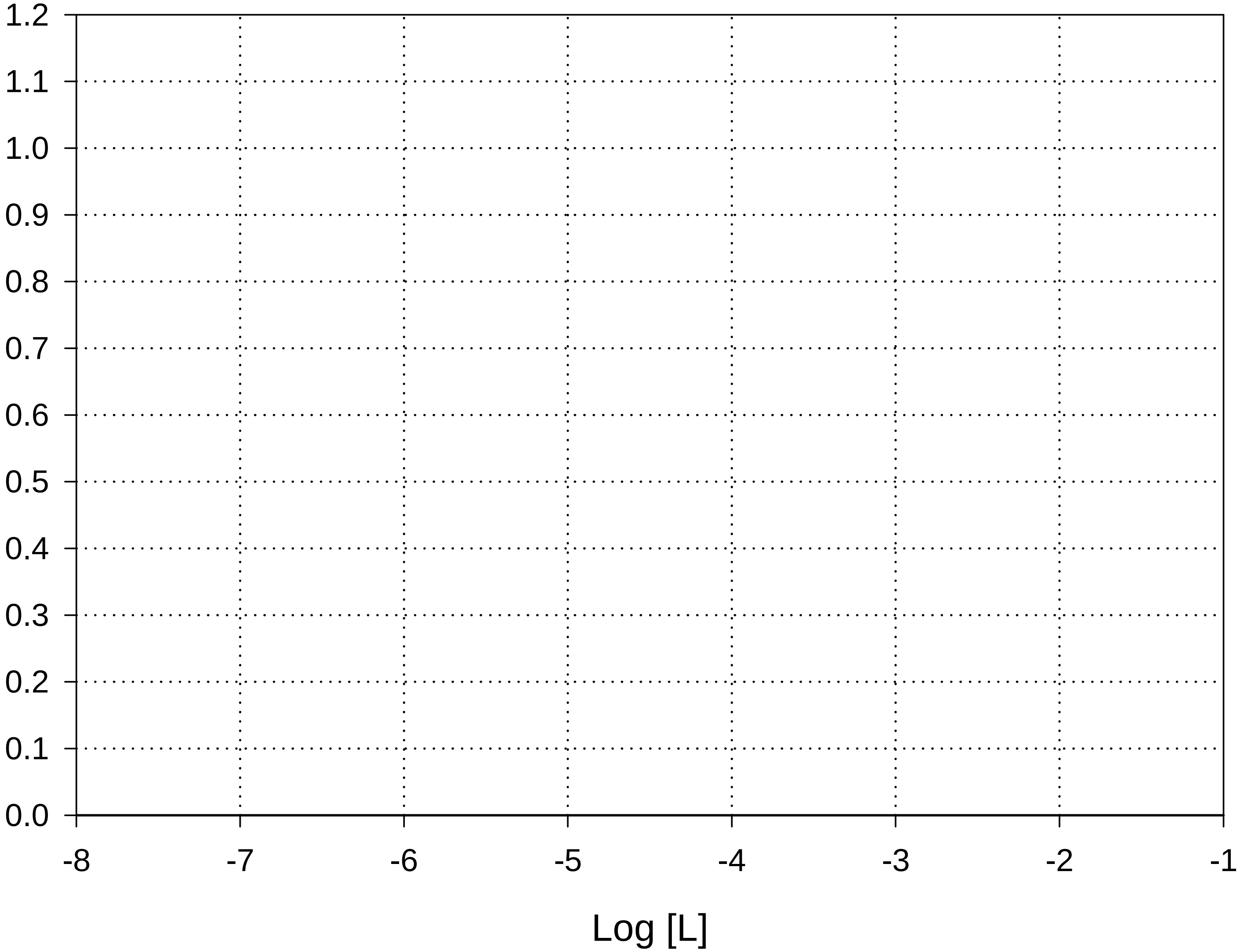
- a. stands for ethylene dioxo-tetraacetic acid
- b. is most commonly used as a pH buffer
- c. is a higly potent carcinogen
- d. all of the above
- **e. none of the above**

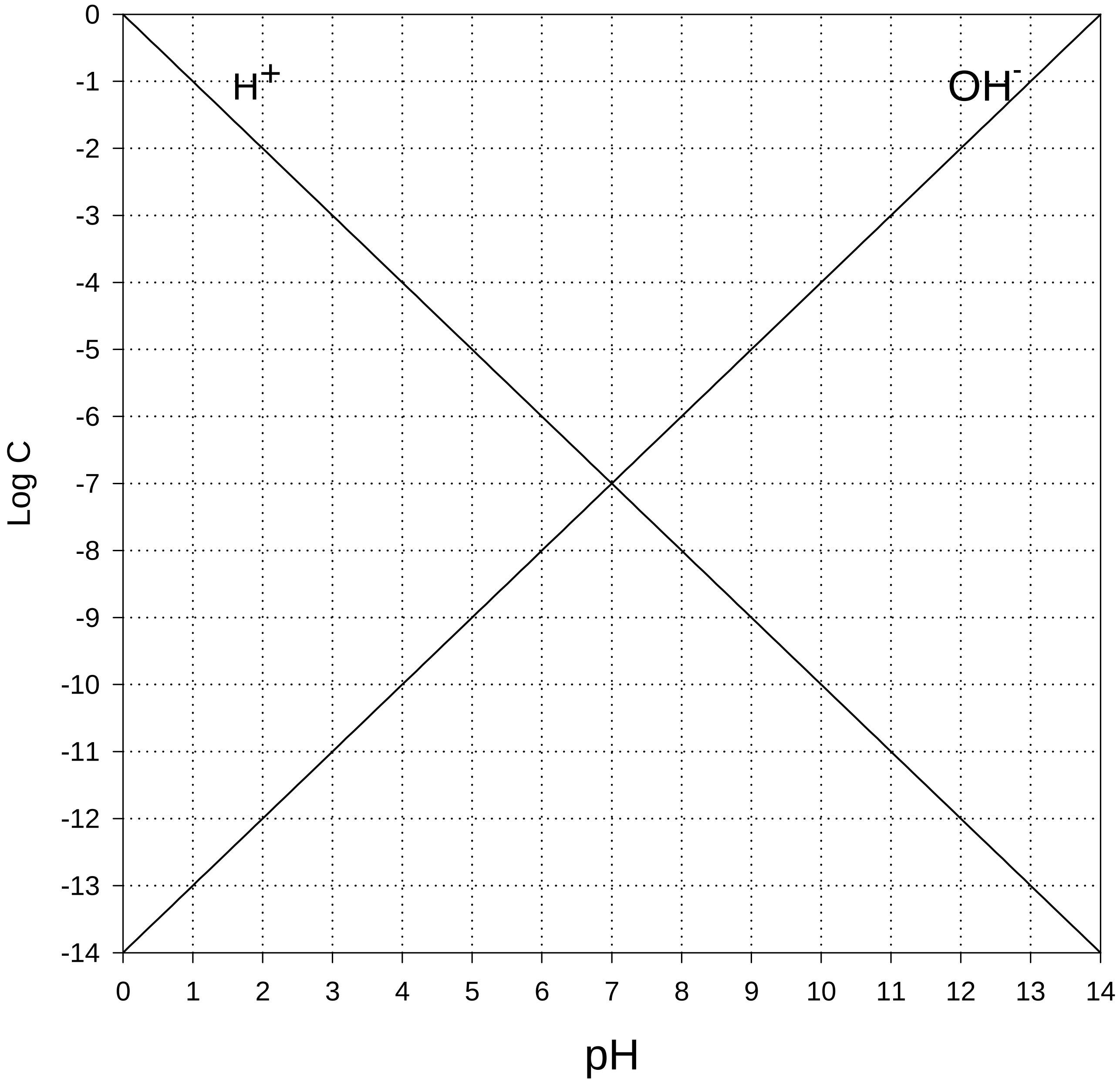
10. As metals become more highly charged, they:

- 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 | pKa |
|---|---|---|
| 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
pH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14