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 $K_H = 10^{-1.5}$ 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).

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:

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

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

$$\approx \frac{K_1}{[H^+]} + 2\frac{K_1 K_2}{[H^+]^2}$$

$$[H^+]^2 - \frac{K_1 K_h p_{CO2}}{Alk}[H^+] - 2\frac{K_1 K_2 K_h p_{CO2}}{Alk} = 0$$

$$[H^+] = \frac{-\left(\frac{K_1 K_h p_{CO2}}{Alk}\right) \pm \sqrt{\left(\frac{K_1 K_h p_{CO2}}{Alk}\right)^2 - 4\left(2\frac{K_1 K_2 K_h p_{CO2}}{Alk}\right)}}{2}$$

or

pH = 7.349

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

$$[H^+] = 10^{-11.35}/0.0001$$
$$[H^+] = 4.47 \times 10^{-8}$$

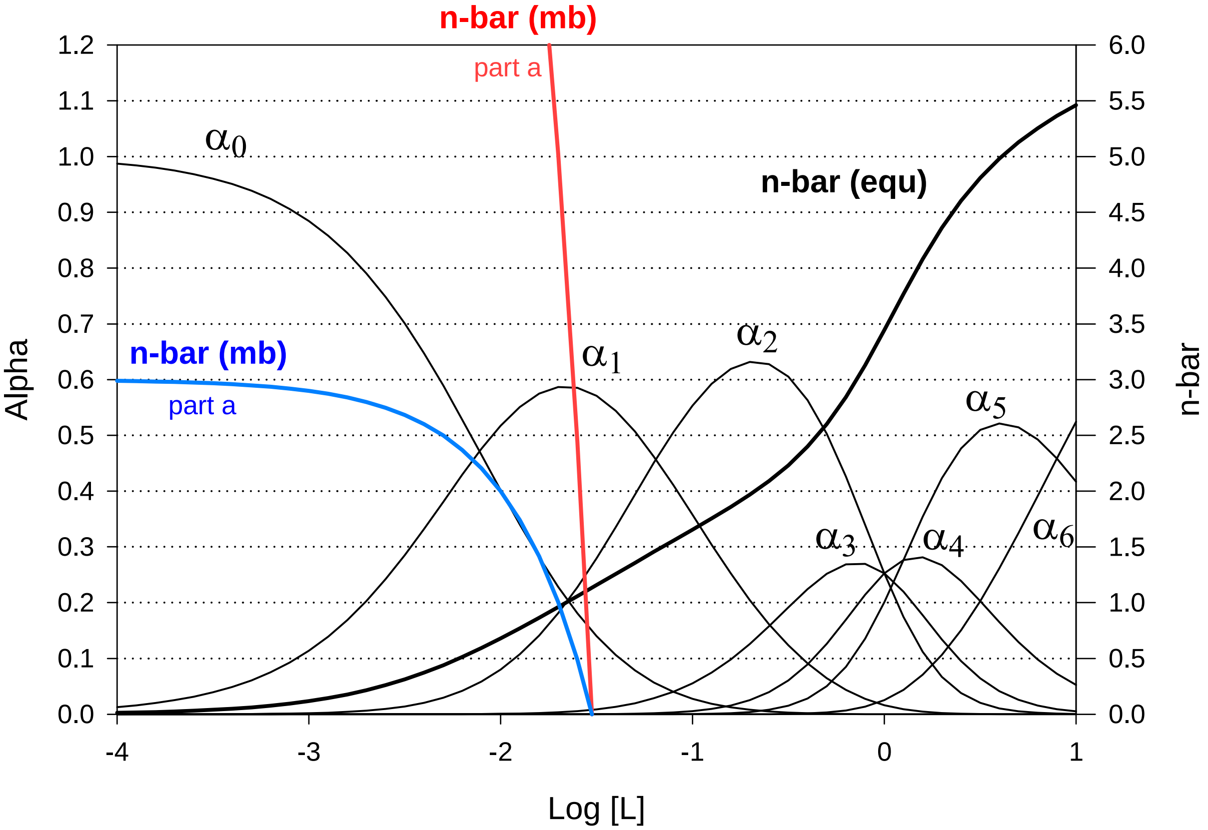
or

pH = 7.35

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


n-bar (mb)
part a
n-bar (mb)
part a
n-bar (equ)
α_0
α_1
α_2
α_3
α_4
α_5
α_6
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
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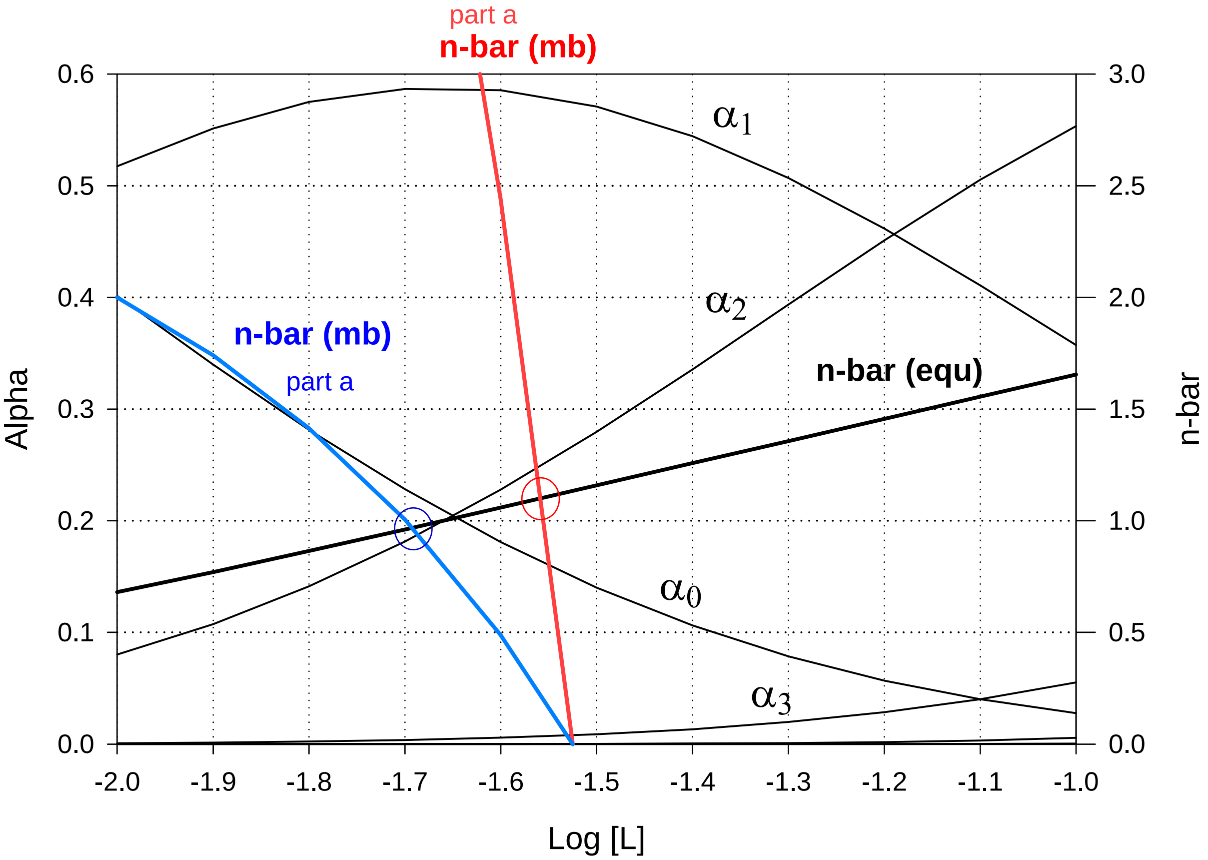
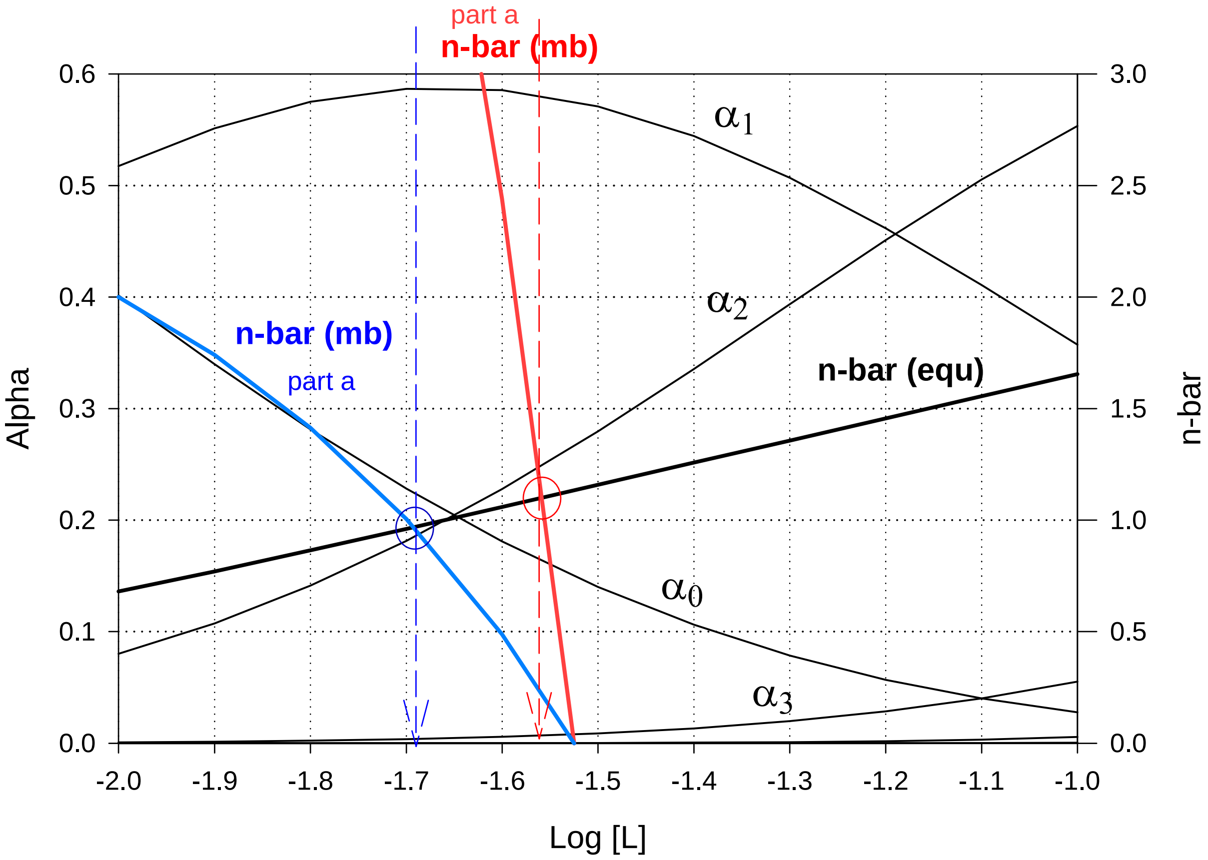
1



part a
n-bar (mb)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Alpha
3.0
2.5
2.0
1.5
1.0
0.5
0.0
n-bar
α_1
α_2
α_0
α_3
n-bar (mb)
part a
n-bar (equ)
-2.0
-1.9
-1.8
-1.7
-1.6
-1.5
-1.4
-1.3
-1.2
-1.1
-1.0
Log [L]



So using the intersections for the n-bar curves we can read off the alpha values and knowing the total Iron is 0.01 M, the individual species concentrations are easily calculated. For Fe(SCN)4 and beyond, the concentrations are too low to estimate, so you can simply list them as zero or below 0.01 mM.

Part A

	Log[SCN]	[SCN]	Fe	FeSCN	Fe(SCN)2	Fe(SCN)3
Alpha	-1.693	0.020	0.225	0.587	0.185	0.004
Conc (M)		0.0203	0.0022	0.0059	0.0018	4E-05

Part B

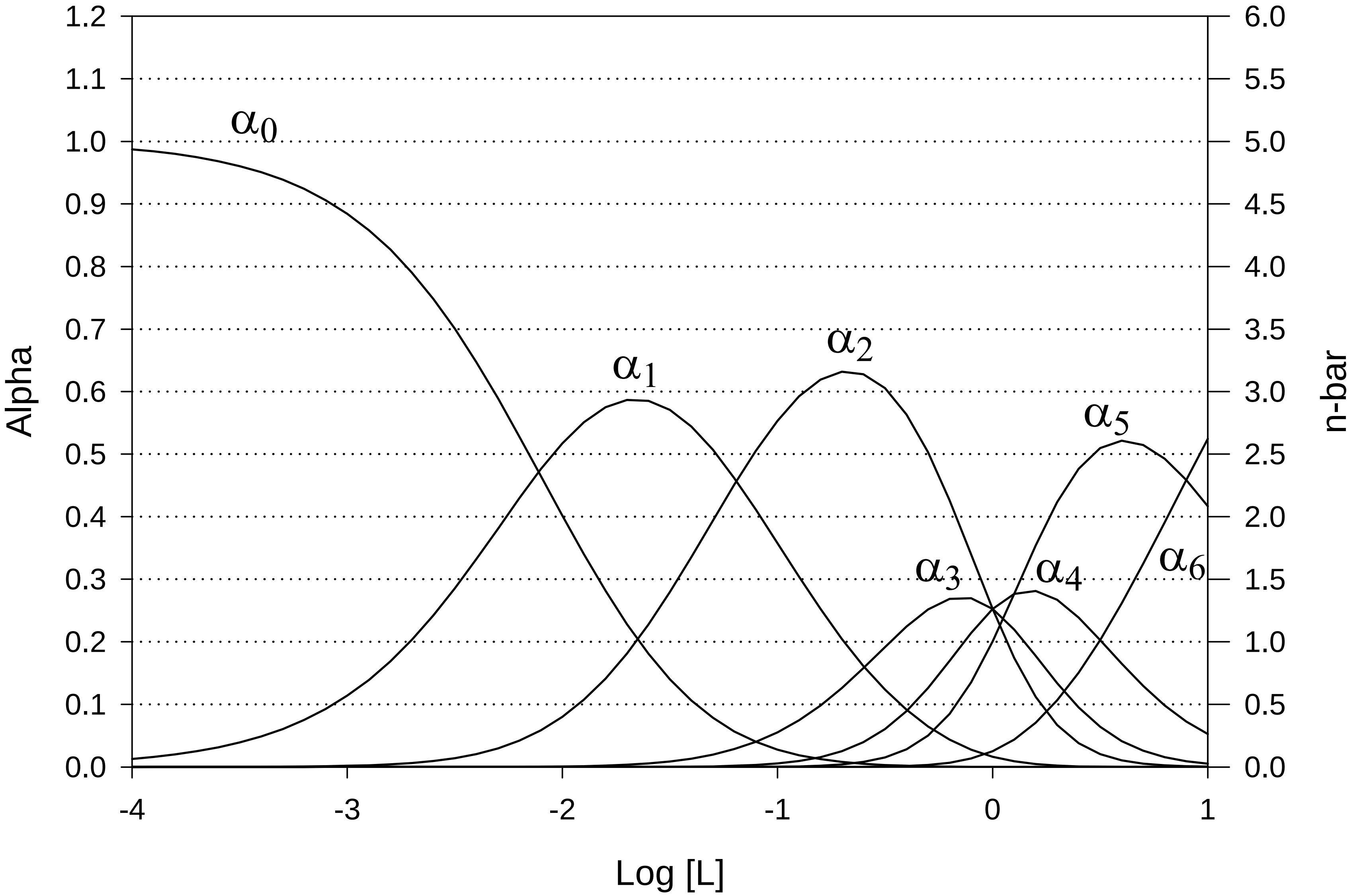
	Log[SCN]	[SCN]	Fe	FeSCN	Fe(SCN)2	Fe(SCN)3
value	-1.57	0.027	0.169	0.581	0.243	0.007
Conc (M)		0.0269	0.00017	0.00058	0.00024	7E-06

Part C.

Here you have a shift to possibly more SCN vs HSCN, but more importantly, there is the higher level of OH at pH 7 which is a competiting ligand. It will also lead to likely precipitation of $Fe(OH)_3$ and depression of the soluble iron concentration. This lowers the C_M value and changes the position of the n-bar (mass balance) curve.

Part D.

Phosphate, especially HPO_4^{-2}, will be another good competing ligand for SCN and OH. It will pull some Fe away from the other complexes and thereby reduce their concentrations. If enough phosphate was present, there might be and $FePO_4$ preciptiate which would further lower C_M and all soluble Fe species.



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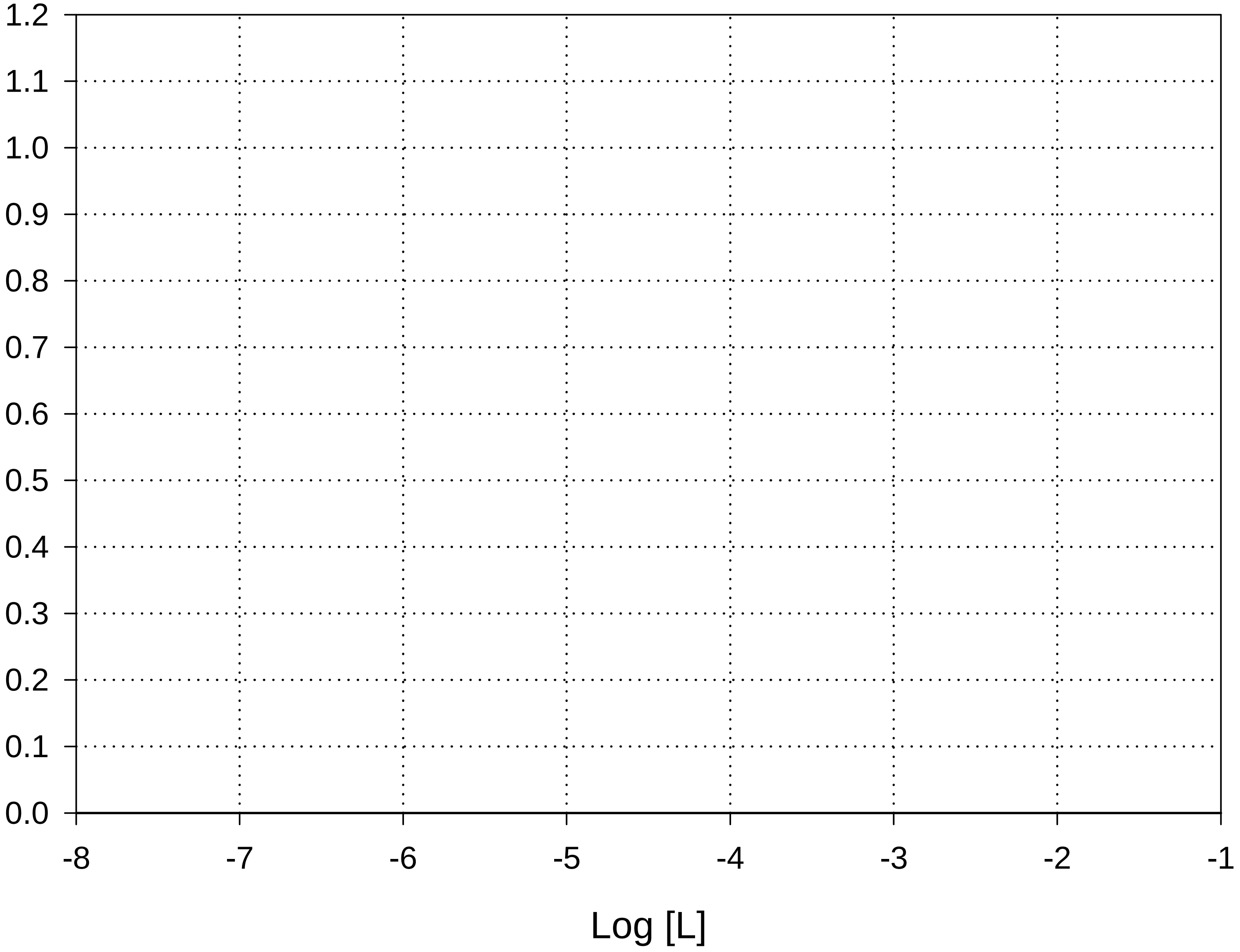
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Alpha
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
n-bar
α_0
α_1
α_2
α_3
α_4
α_5
α_6
-4
-3
-2
-1
0
1
Log [L]

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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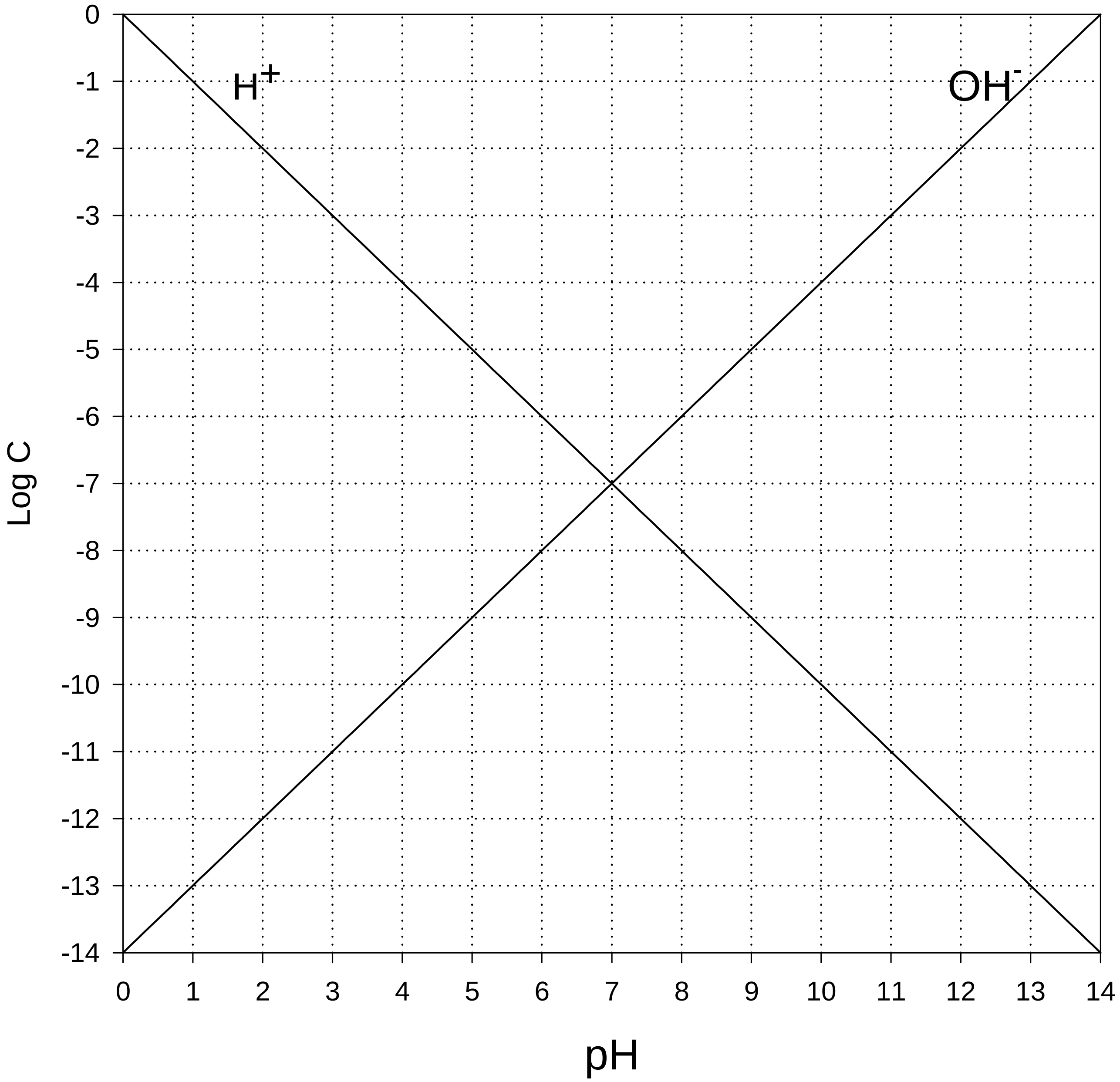
-8
-7
-6
-5
-4
-3
-2
-1
Log [L]


H+
OH-
Log C
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-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0
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3
4
5
6
7
8
9
10
11
12
13
14
pH