Updated: 22 March 2020

Print version

CEE 680: Water Chemistry

Lecture #30

Coordination Chemistry: case studies

(Stumm & Morgan, Chapt.6: pg.305-319)

Benjamin; Chapter 8.1-8.6

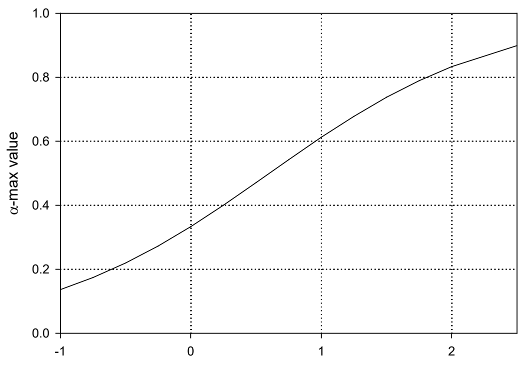
Summary of a few general rules

- At the intersection of sequential alphas, α_i and α_{i+1} :

$$Log[L] = pK_{i+1}$$

- At the peak of an intermediate alpha, α_i , where $i \neq 0$, *or the coordination number*

$$Log[L] = \frac{1}{2}(pK_i + pK_{i+1})$$



$LogK_i - LogK_{i+1}$

  - This peak is also usually near intersection of the previous and following alphas (i.e., α_{i-1} and α_{i+1}), and its maximum height is estimated from:

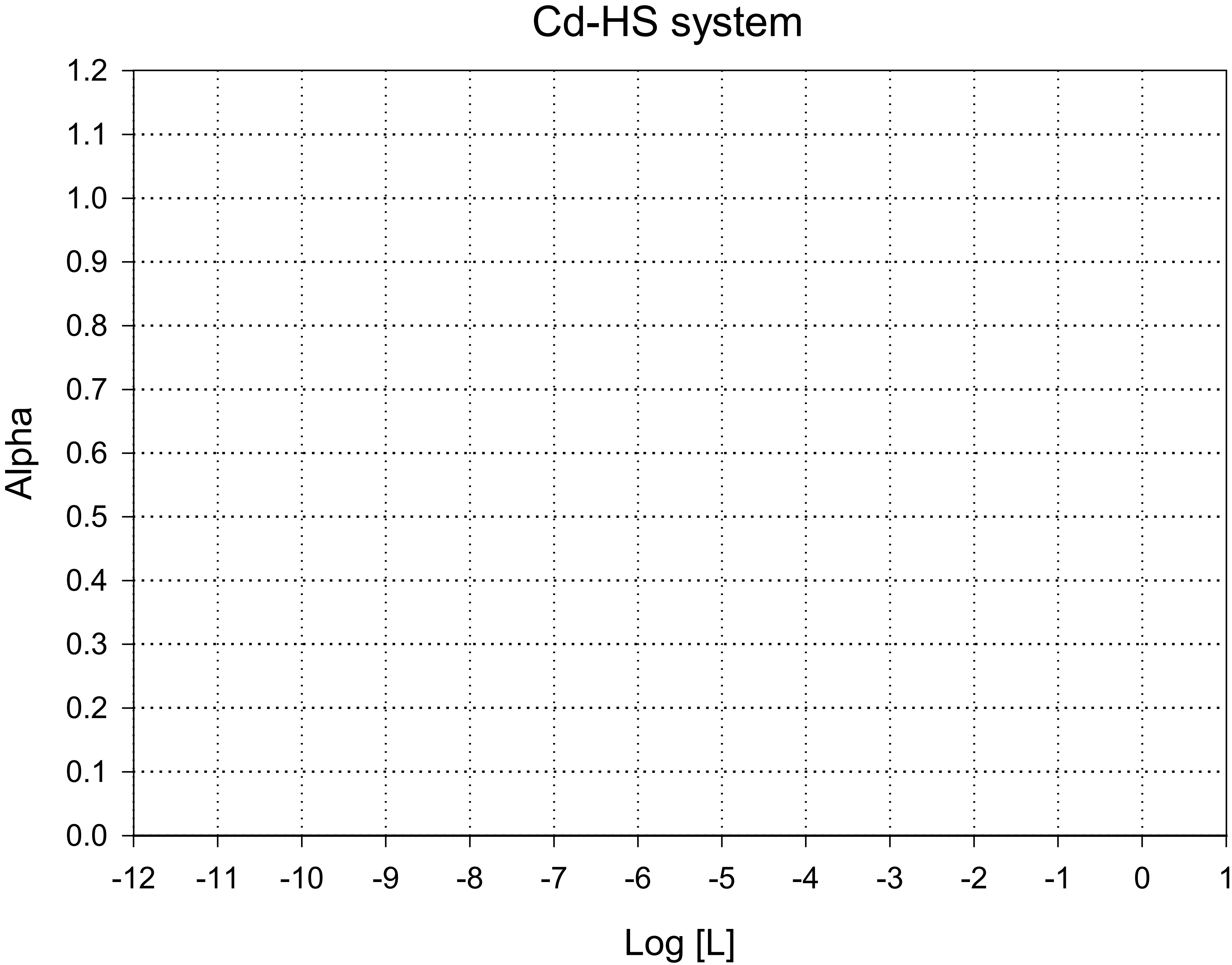
Cadmium Complexes

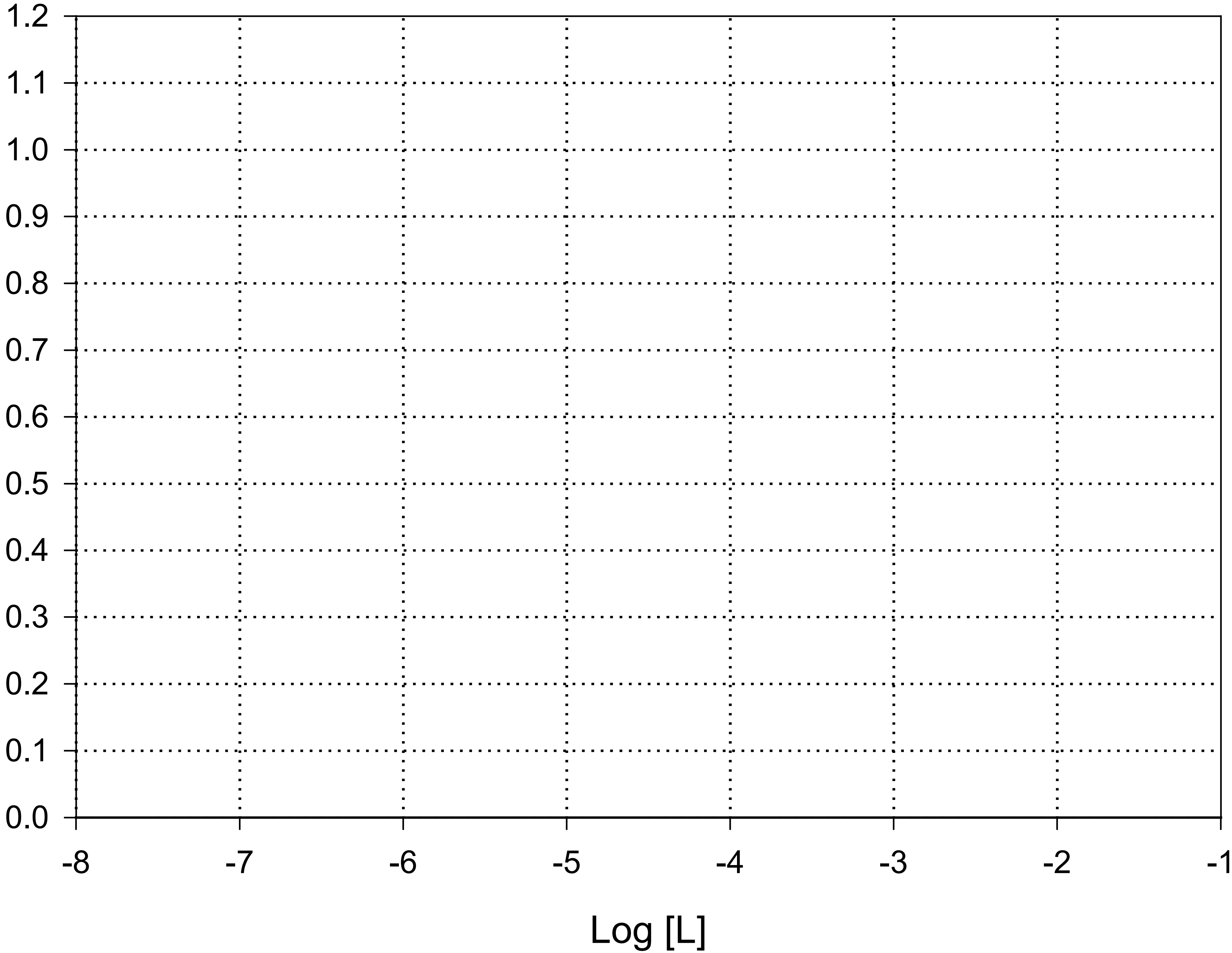
- Bisulfide Ligand

Species	log K	Log Beta
CdL	Log K_1 = 10.17	Log β_1 = 10.17
CdL_2	Log K_2 = 6.36	Log β_2 = 16.53
CdL_3	Log K_3 = 2.18	Log β_3 = 18.71
CdL_4	Log K_4 = 2.19	Log β_4 = 20.90

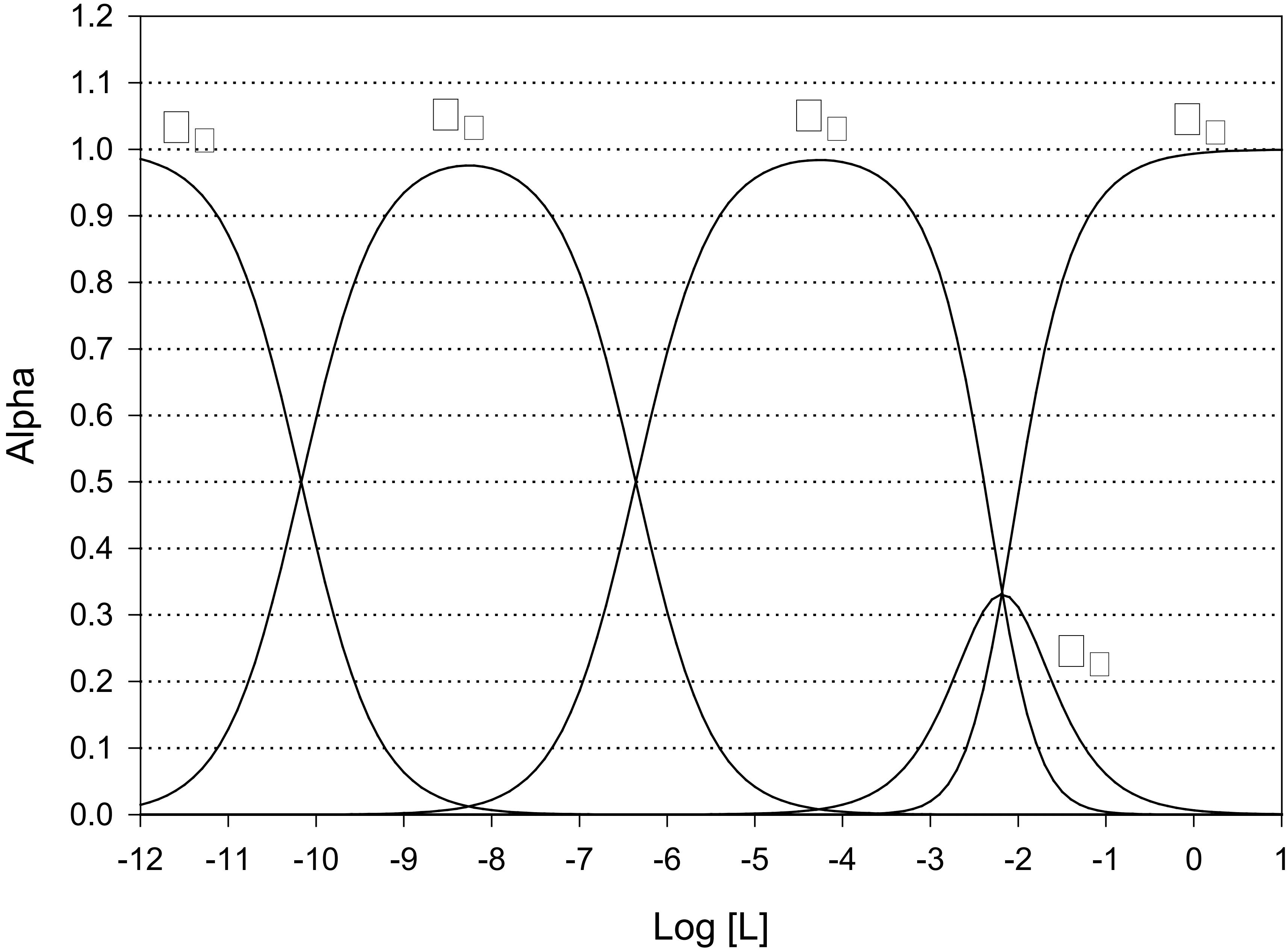
- Cyanide Ligand

Species	log K	Log Beta
CdL	Log K_1 = 5.32	Log β_1 = 5.32
CdL_2	Log K_2 = 5.05	Log β_2 = 10.37
CdL_3	Log K_3 = 4.46	Log β_3 = 14.83
CdL_4	Log K_4 = 3.46	Log β_4 = 18.29

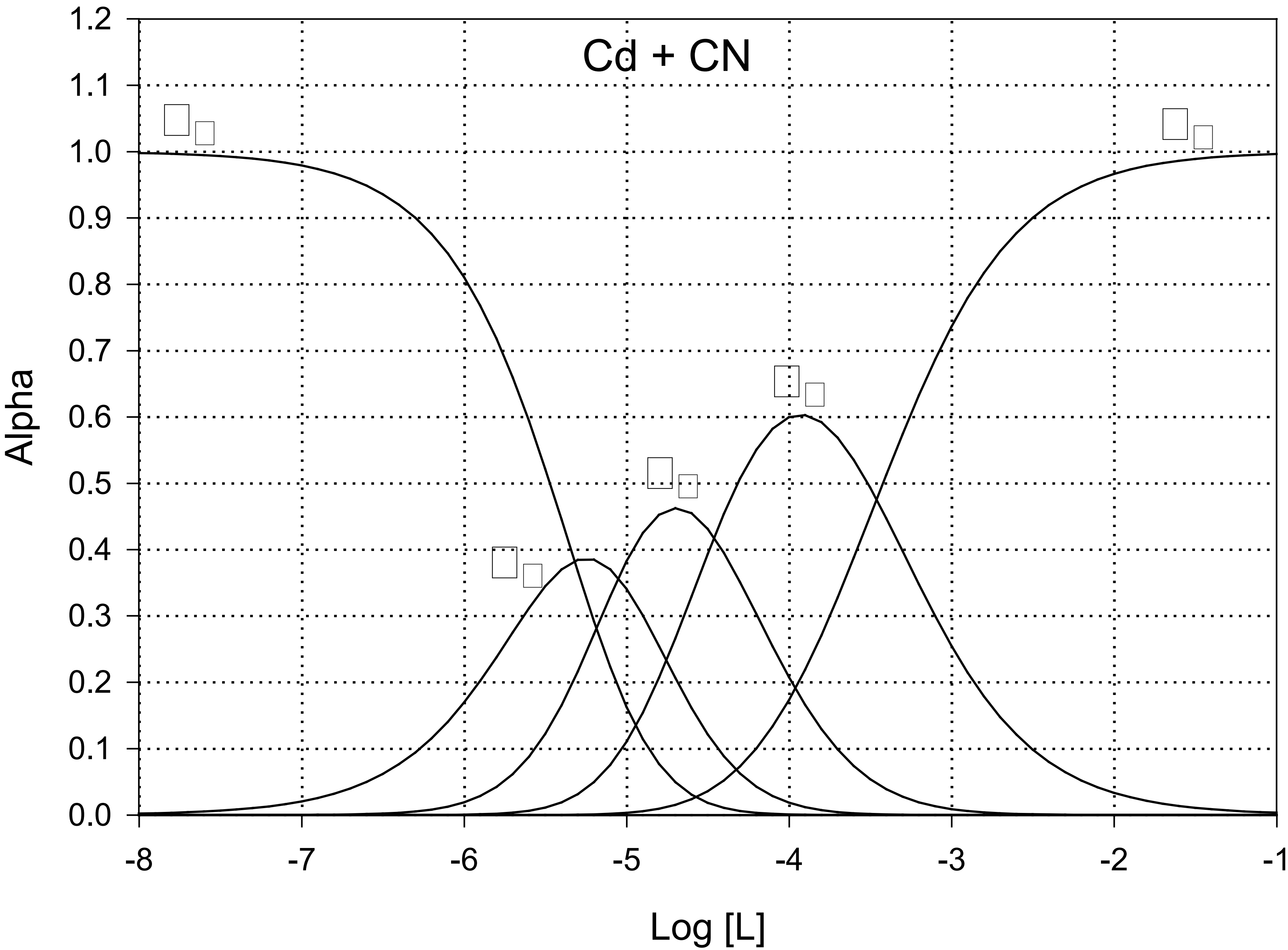

Cd-HS system
Alpha
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1
Log [L]


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

Cd-HS system



Alpha
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
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1



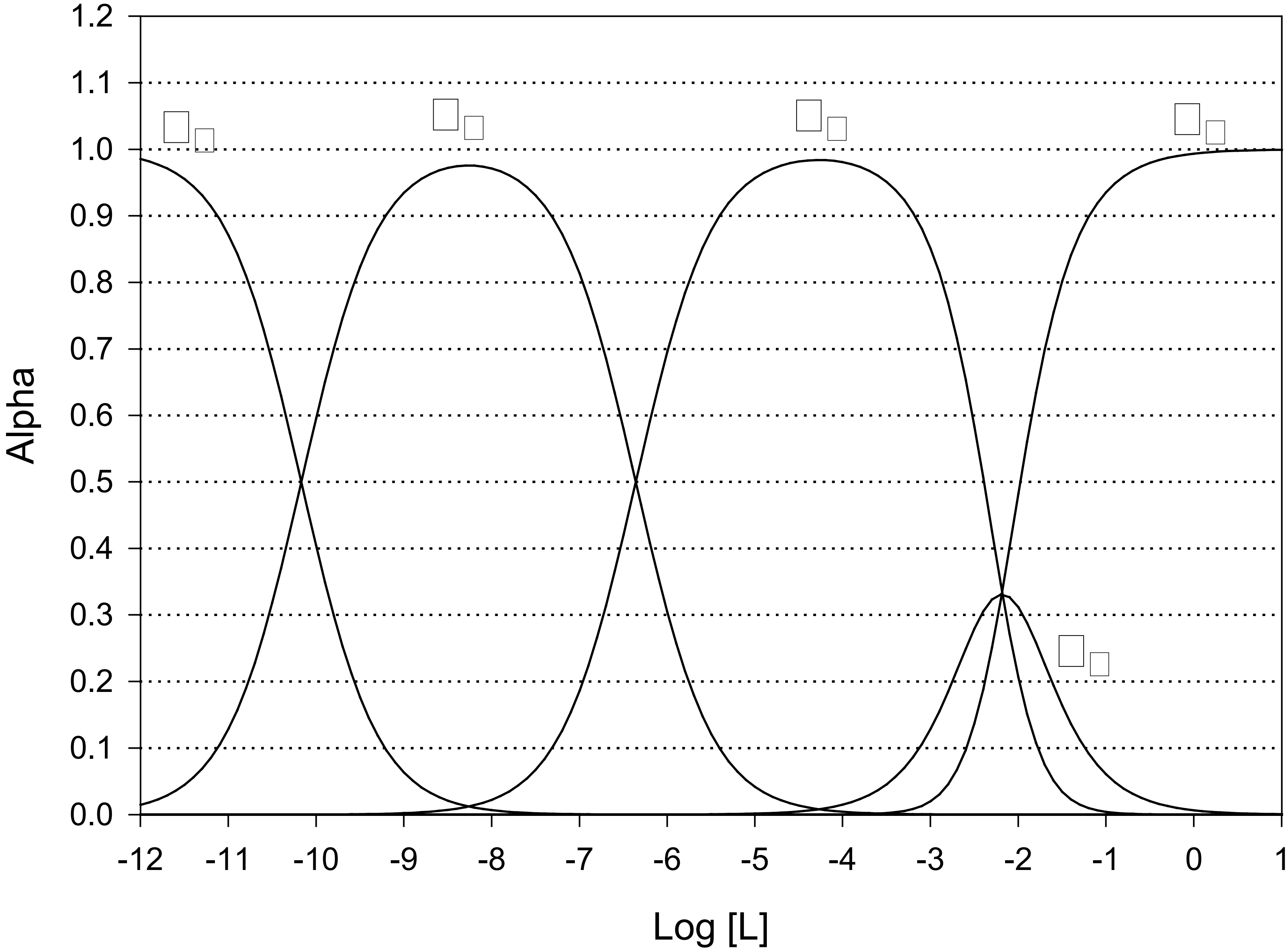
Cd + CN
Alpha
Log [L]
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-8
-7
-6
-5
-4
-3
-2
-1

Cadmium Bisulfide

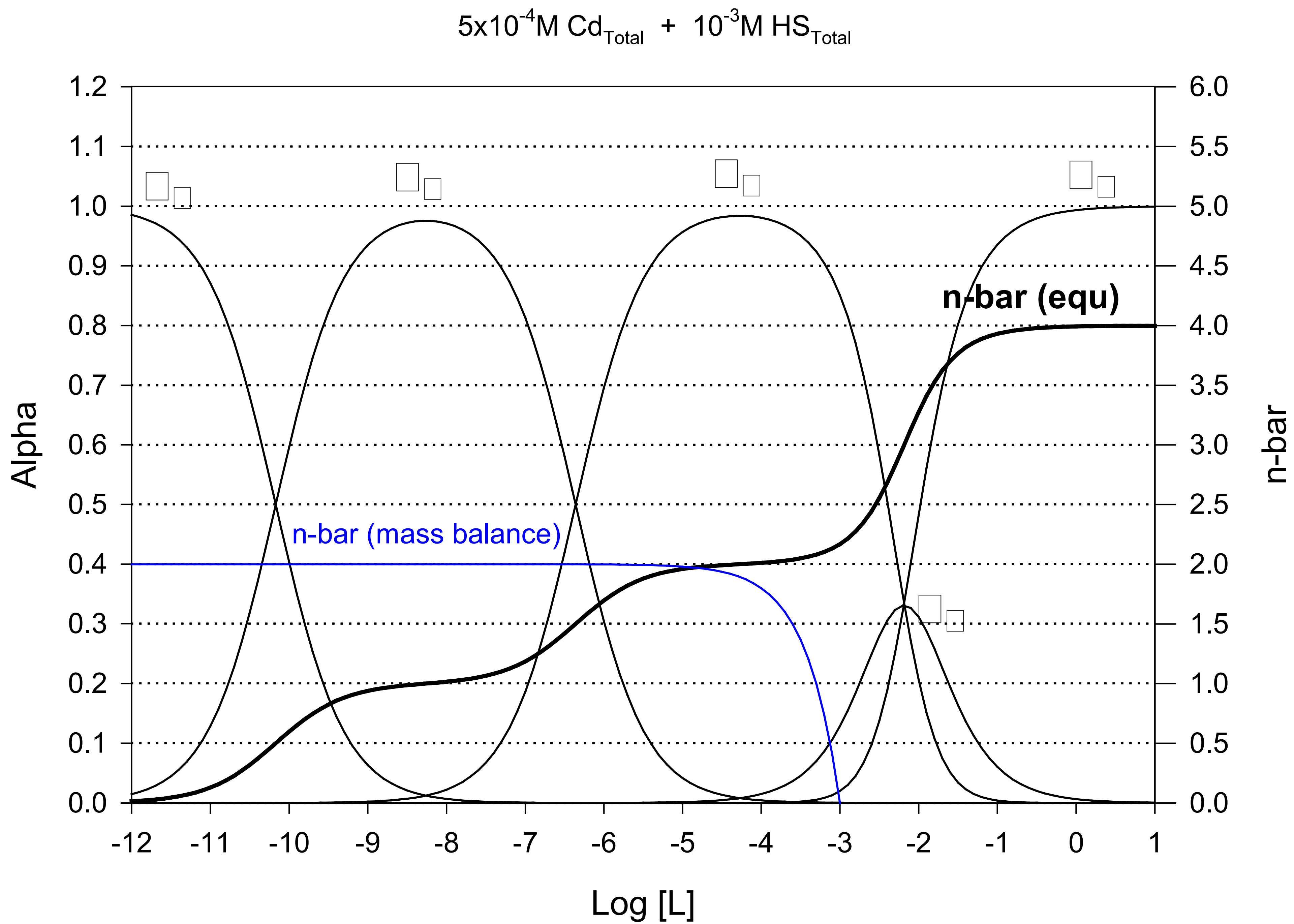
Species	log K	Log Beta
CdL	Log K_1 = 10.17	Log β_1 = 10.17
CdL_2	Log K_2 = 6.36	Log β_2 = 16.53
CdL_3	Log K_3 = 2.18	Log β_3 = 18.71
CdL_4	Log K_4 = 2.19	Log β_4 = 20.90

- Specific Problem
  - 5 x 10^{-4} M Cd total
  - 10^{-3} M HS total

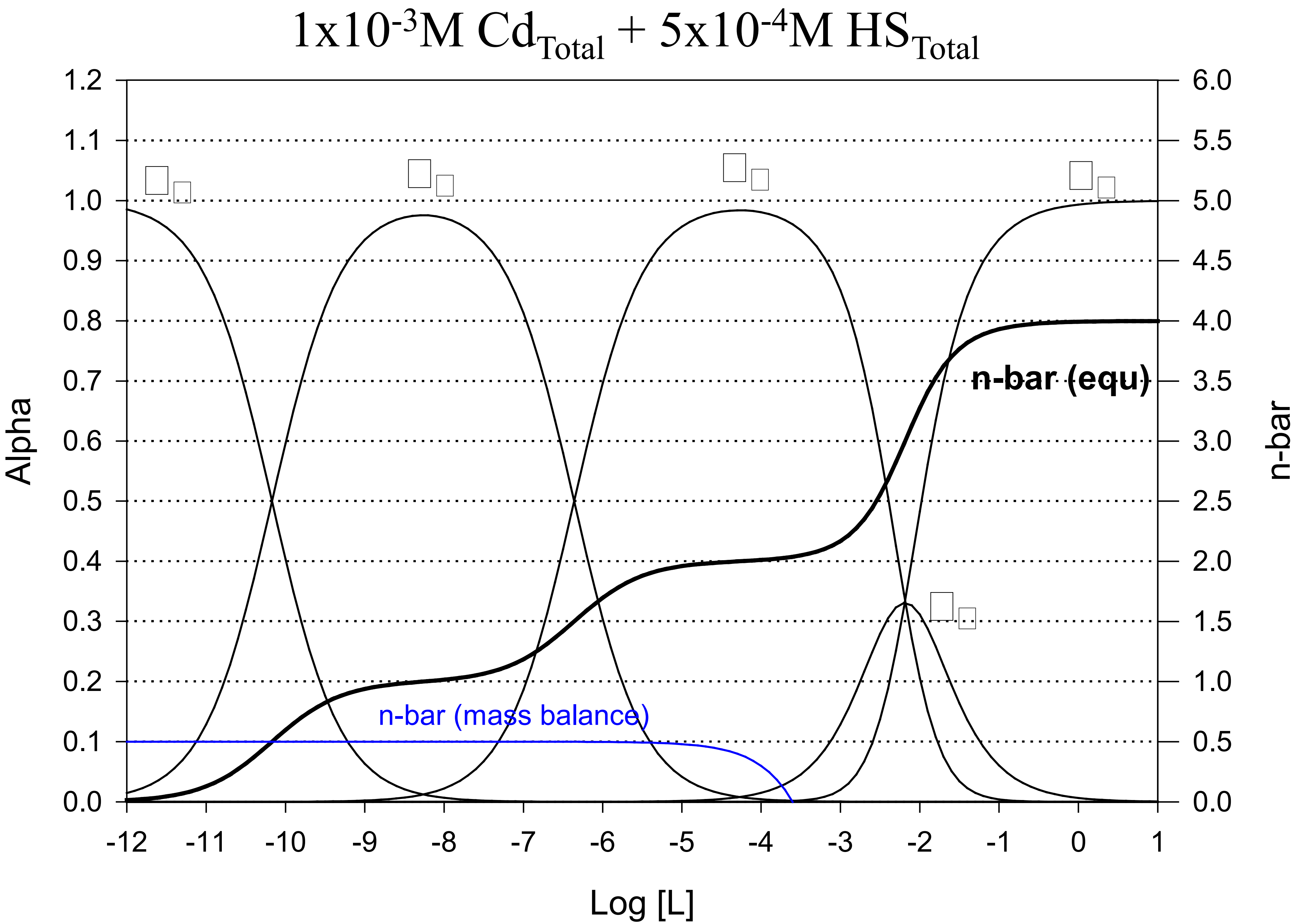
Cd-HS system



Alpha
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
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1



5x10-4M CdTotal + 10-3M HSTotal
Alpha
n-bar
Log [L]
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
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1

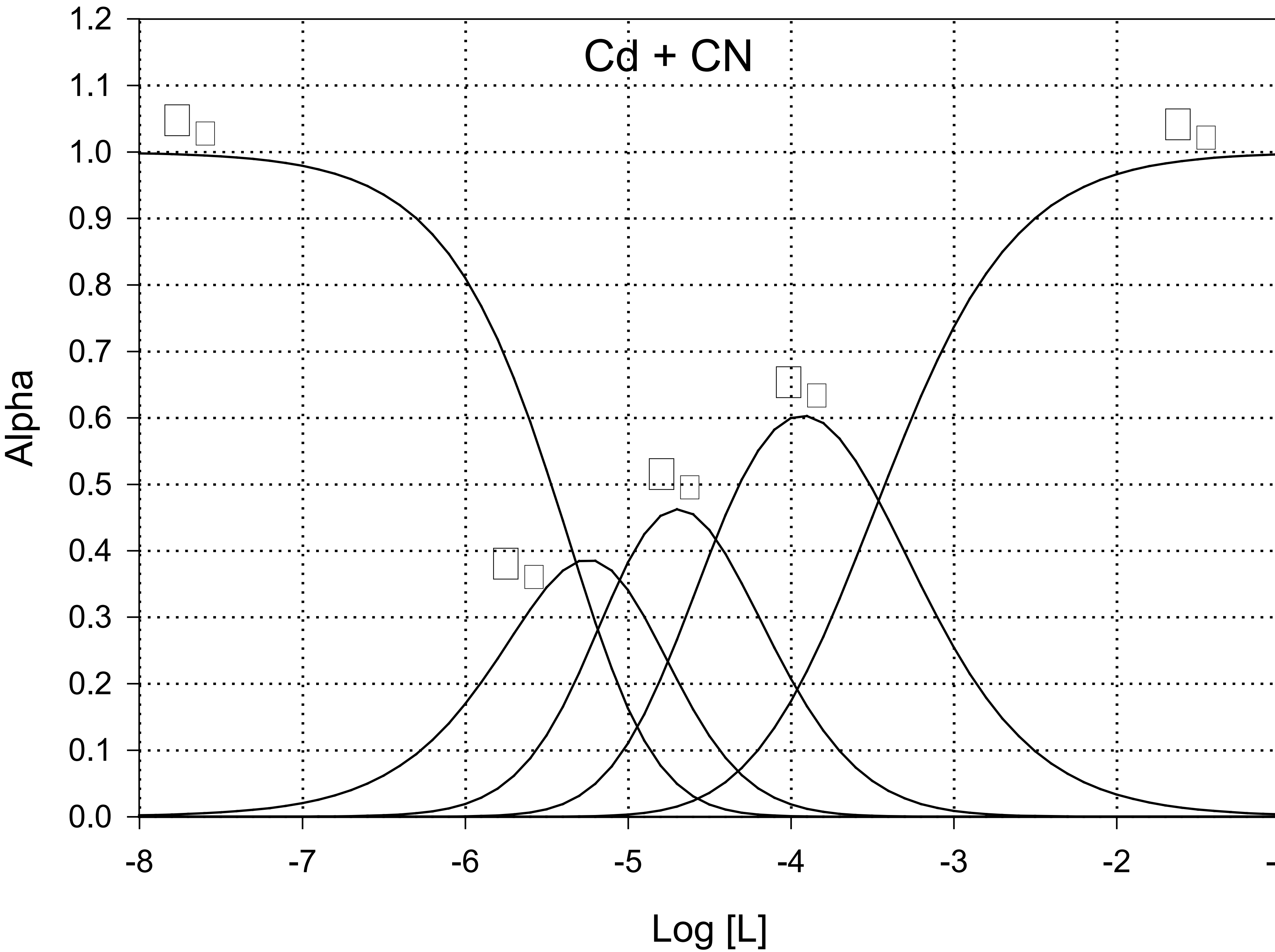


$1x10^{-3}M\ Cd_{Total} + 5x10^{-4}M\ HS_{Total}$
Alpha
n-bar
n-bar (equ)
n-bar (mass balance)
Log [L]
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-12 -11 -10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1

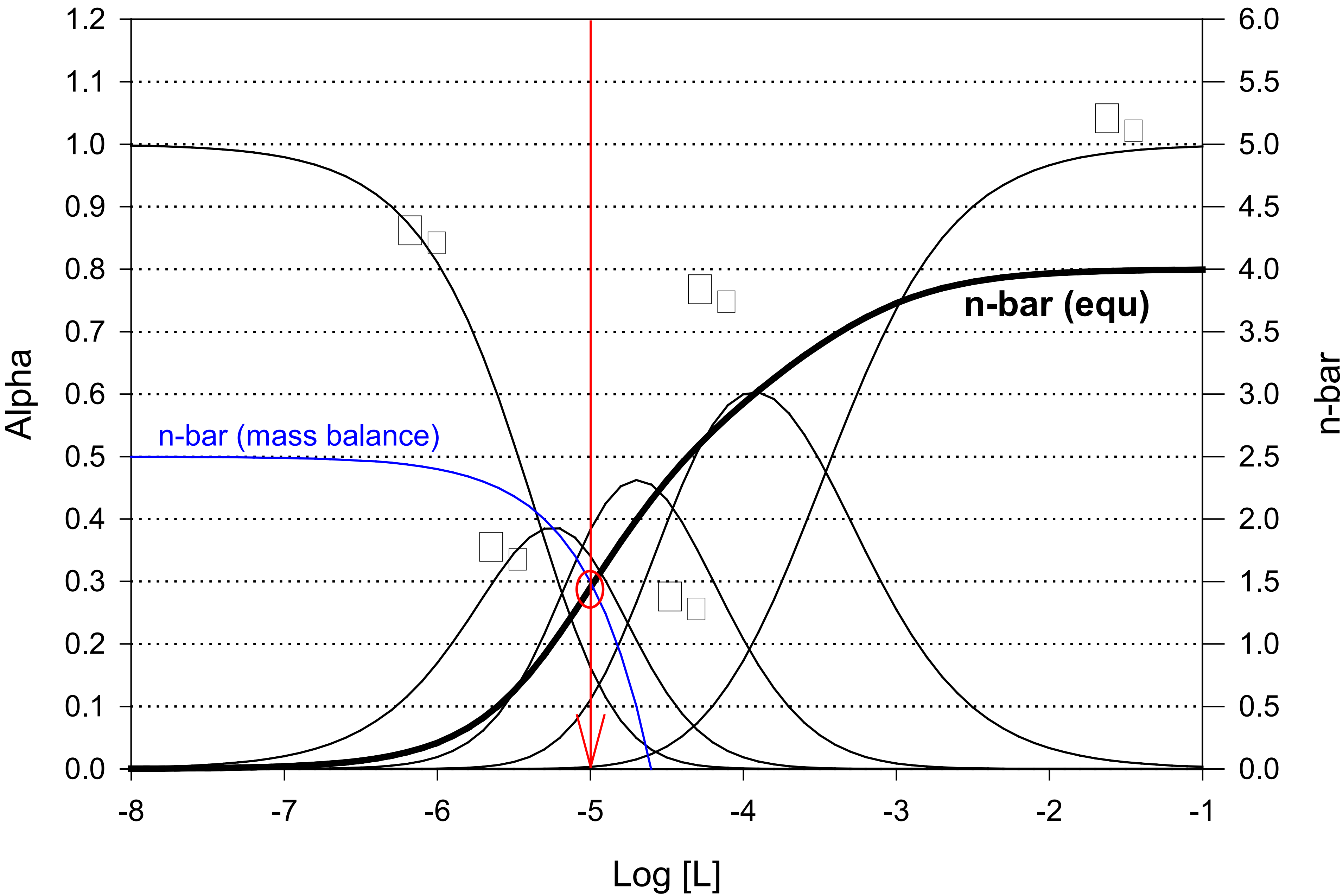
Cadmium Cyanide

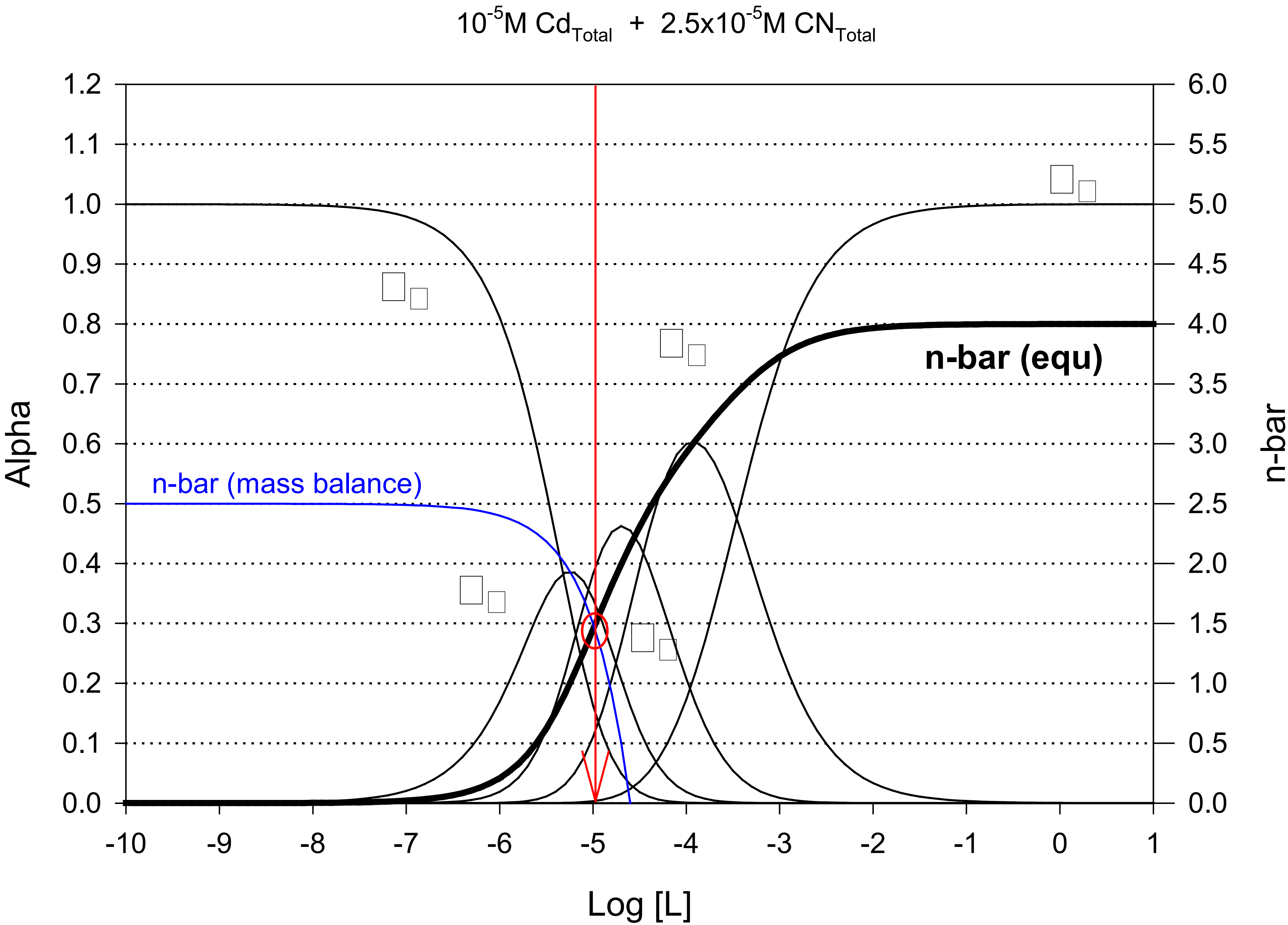
Species	log K	Log Beta
CdL	Log K_1 = 5.32	Log β_1 = 5.32
CdL_2	Log K_2 = 5.05	Log β_2 = 10.37
CdL_3	Log K_3 = 4.46	Log β_3 = 14.83
CdL_4	Log K_4 = 3.46	Log β_4 = 18.29

- Specific Problem
  - 10^{-5} M Cd total
  - 2.5 x 10^{-5}M CN total


Cd + CN
Alpha
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
-8
-7
-6
-5
-4
-3
-2
-1

10^{-5}M Cd_{Total} + $2.5x10^{-5}$M CN_{Total}



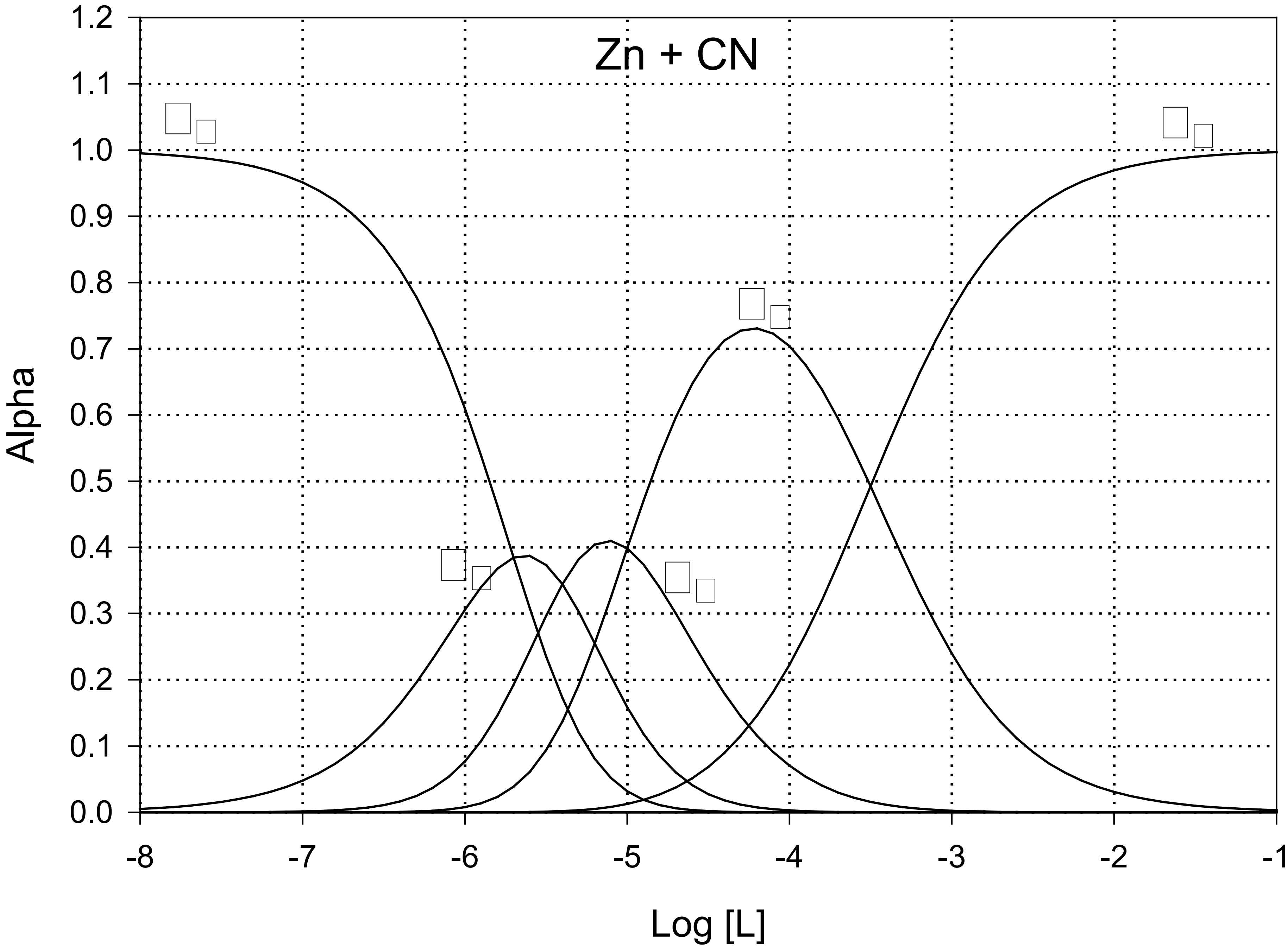


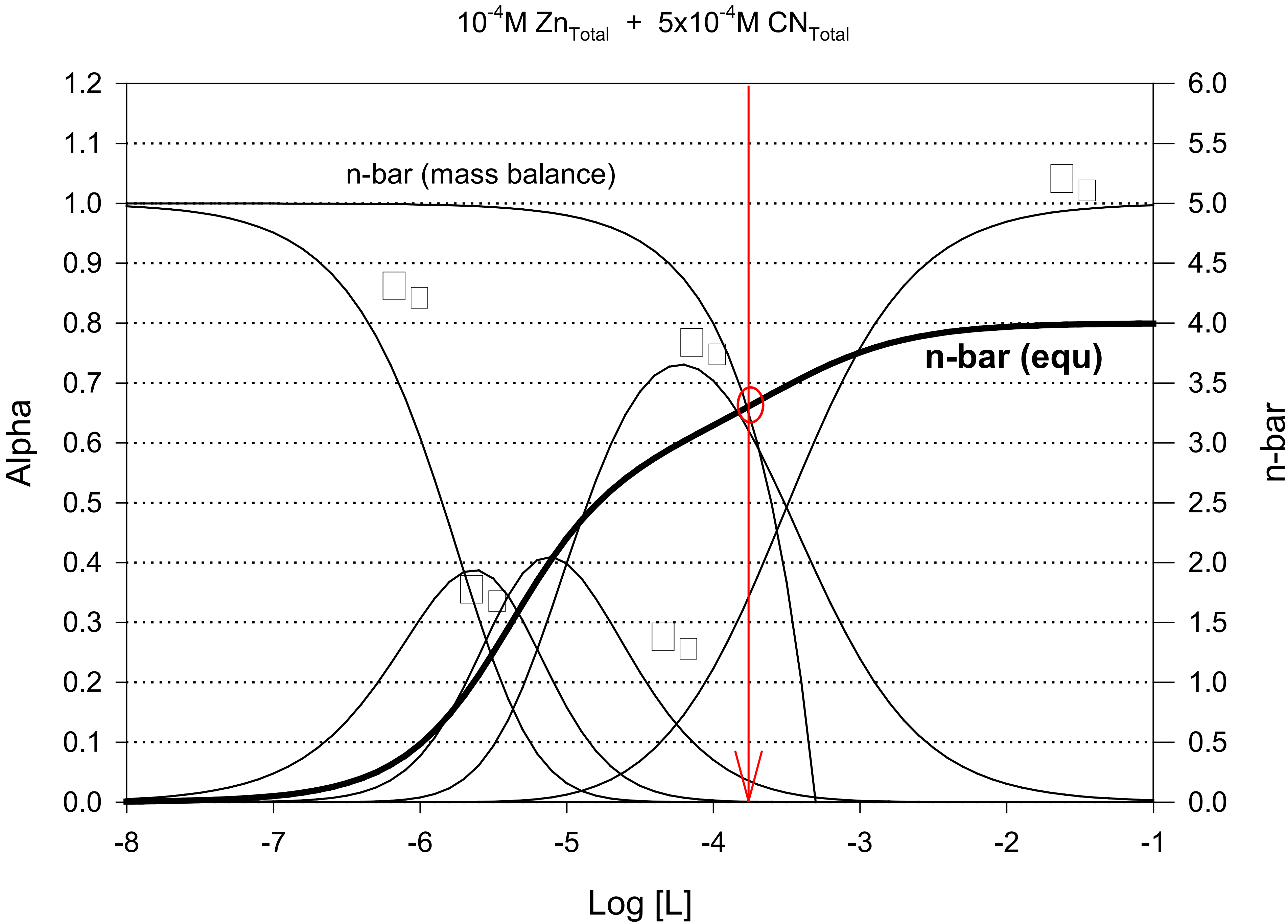
10^{-5}M Cd_{Total} + $2.5x10^{-5}$M CN_{Total}
Alpha
n-bar
n-bar (mass balance)
n-bar (equ)
Log [L]
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1

Zinc Cyanide

Species	Betas
ZnL	Log β_1 = 5.7
ZnL_2	Log β_2 = 11.1
ZnL_3	Log β_3 = 16.1
ZnL_4	Log β_4 = 19.6

- Specific Problem
  - 10^{-4} M Zn total
  - 5 x 10^{-4}M CN total

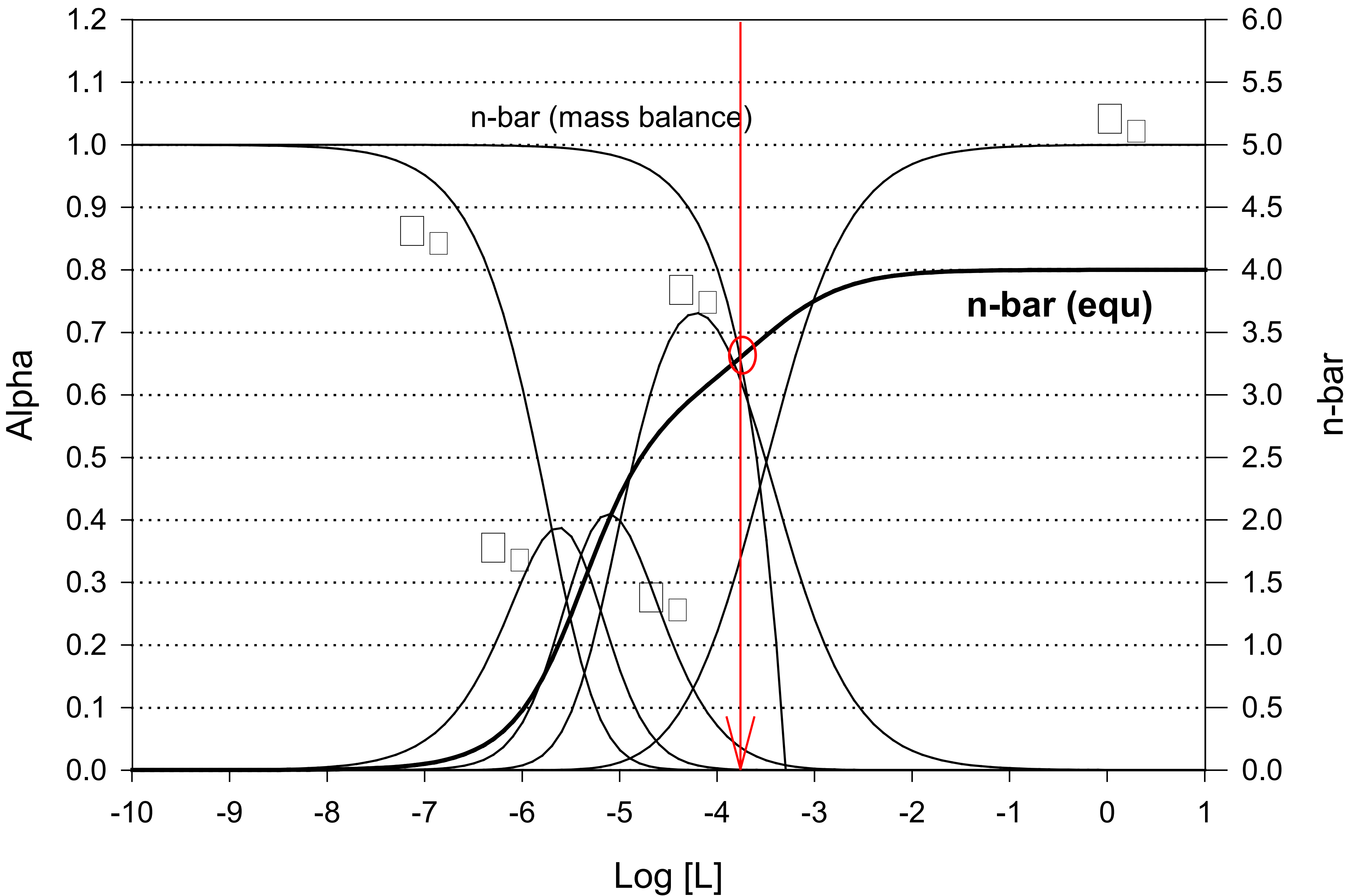

Zn + CN
Alpha
Log [L]
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-8
-7
-6
-5
-4
-3
-2
-1

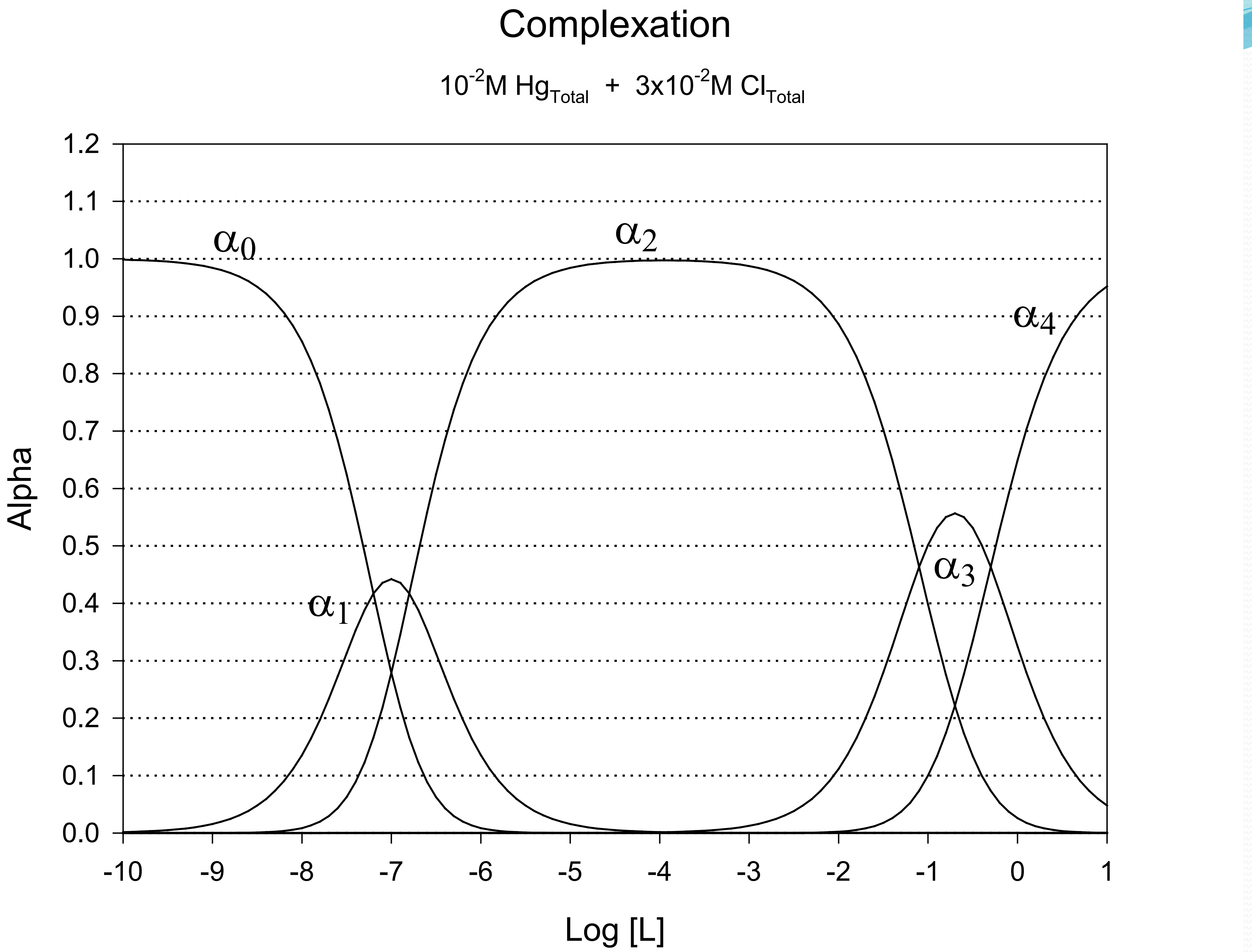


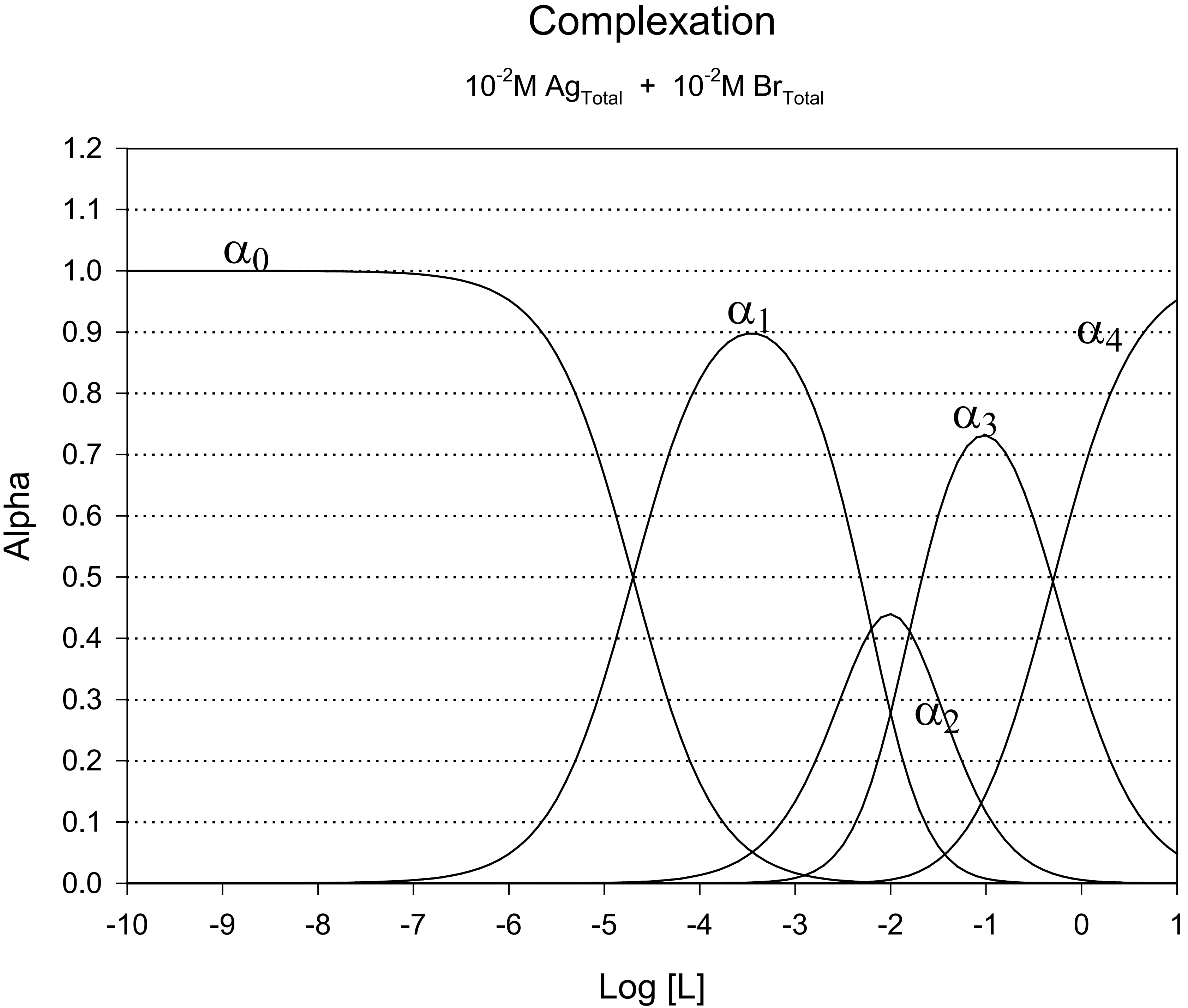
10^-4 M Zn_Total + 5x10^-4 M CN_Total
n-bar (mass balance)
n-bar (equ)
Alpha
n-bar
Log [L]
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-8
-7
-6
-5
-4
-3
-2
-1

Complexation

10^{-4}M Zn_{Total} + $5x10^{-4}$M CN_{Total}




Complexation
10^{-2}M Hg_{Total} + $3x10^{-2}$M Cl_{Total}
Alpha
Log [L]
α_0
α_1
α_2
α_3
α_4
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
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1



Complexation
10-2M Ag Total + 10-2M Br Total
Alpha
Log [L]
α0
α1
α2
α3
α4
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
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1

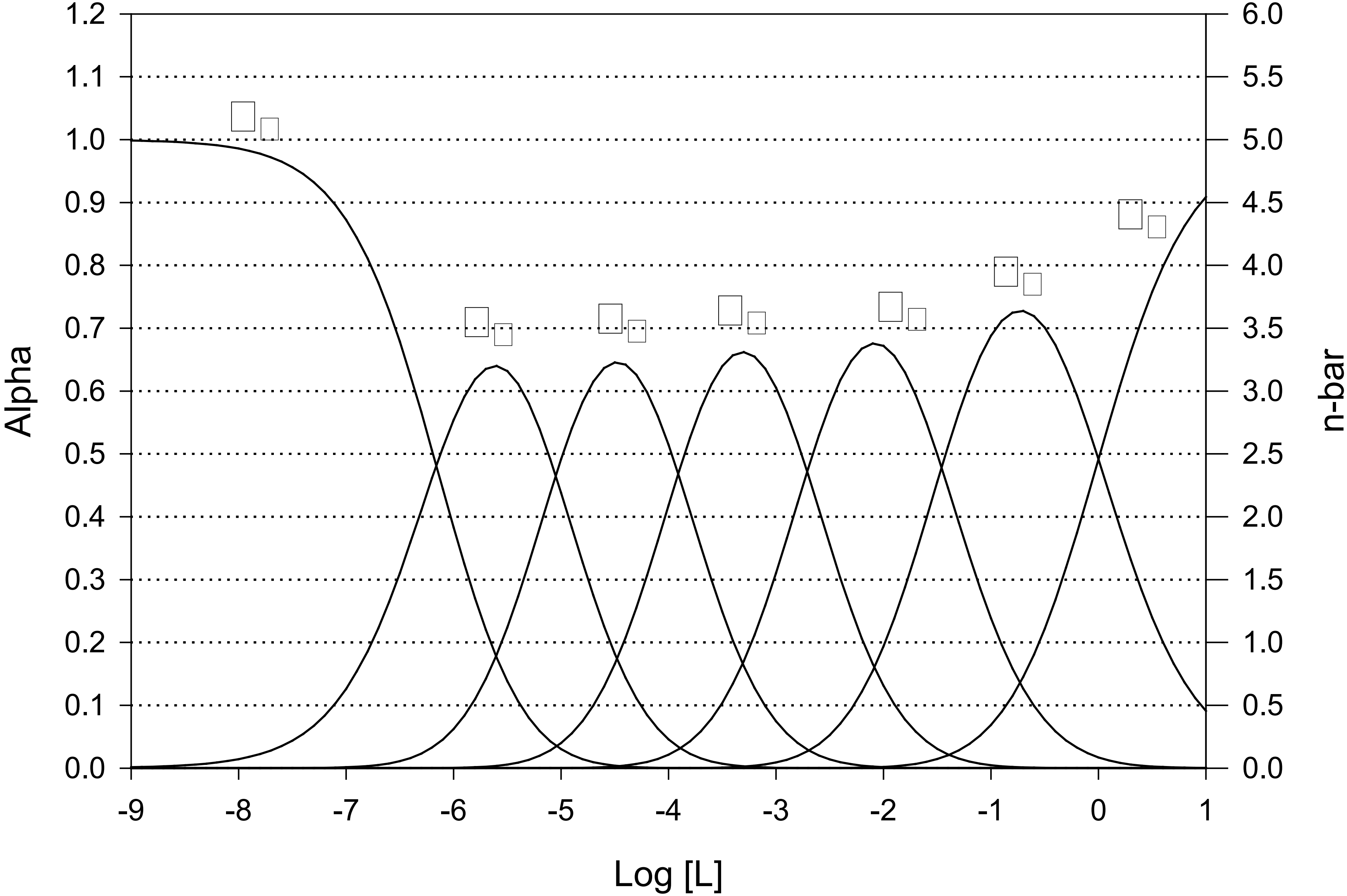
Aluminum Fluoride system

- Significance
  - Aluminum in natural waters
  - Aluminum in coagulation
- Thermodynamic Values: Smith & Martel (Benjamin)
  - Log K_1 = 6.16 (7.01)
  - Log K_2 = 5.05 (5.74)
  - Log K_3 = 3.91 (4.27)
  - Log K_4 = 2.71 (2.70)
  - Log K_5 = 1.46 (1.08)
  - Log K_6 = 0 (-0.3)
- Now calculate alpha's

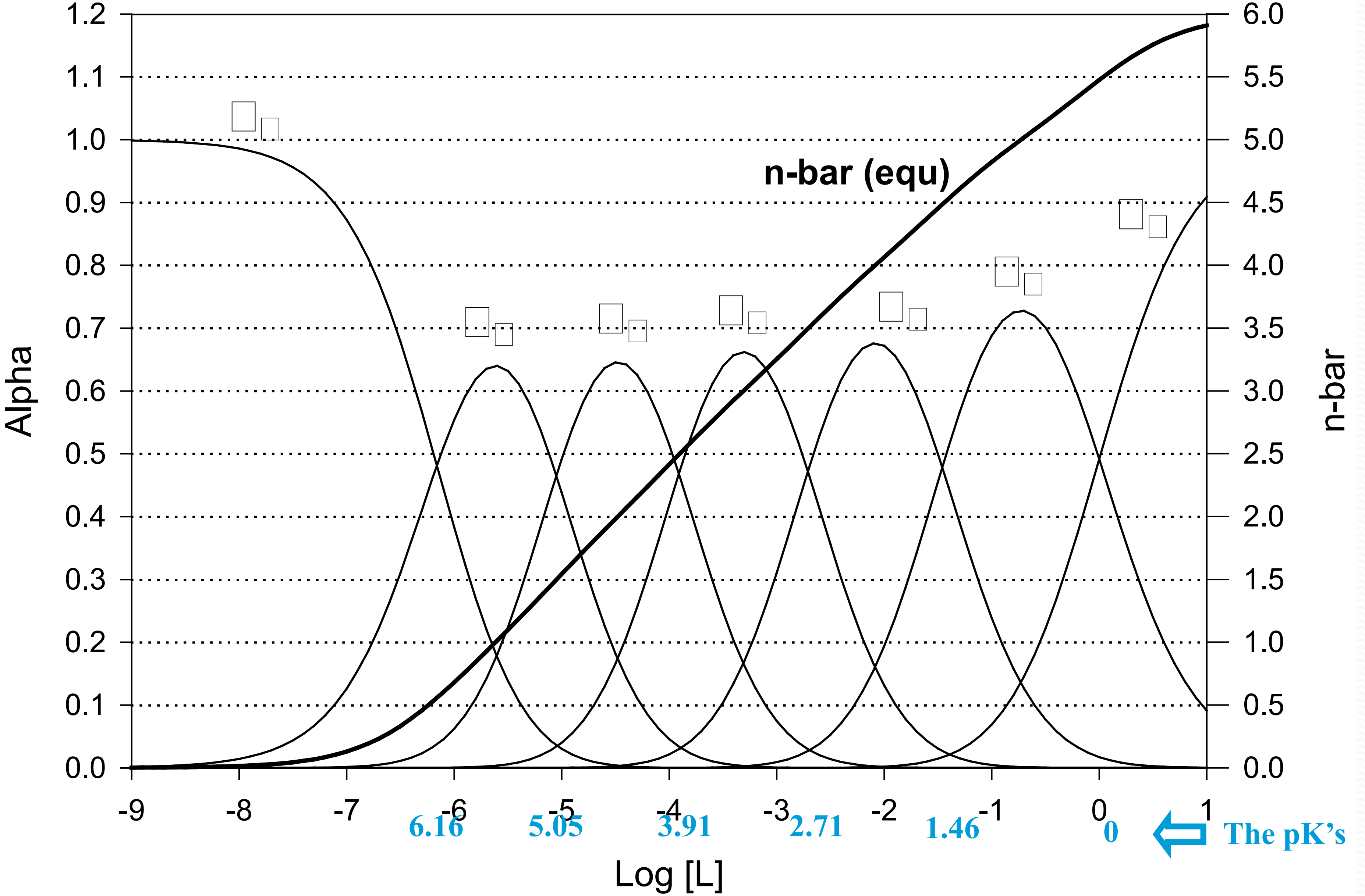
$$\alpha_0 \equiv \frac{[M]}{C_M} = \left(1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n\right)^{-1}$$

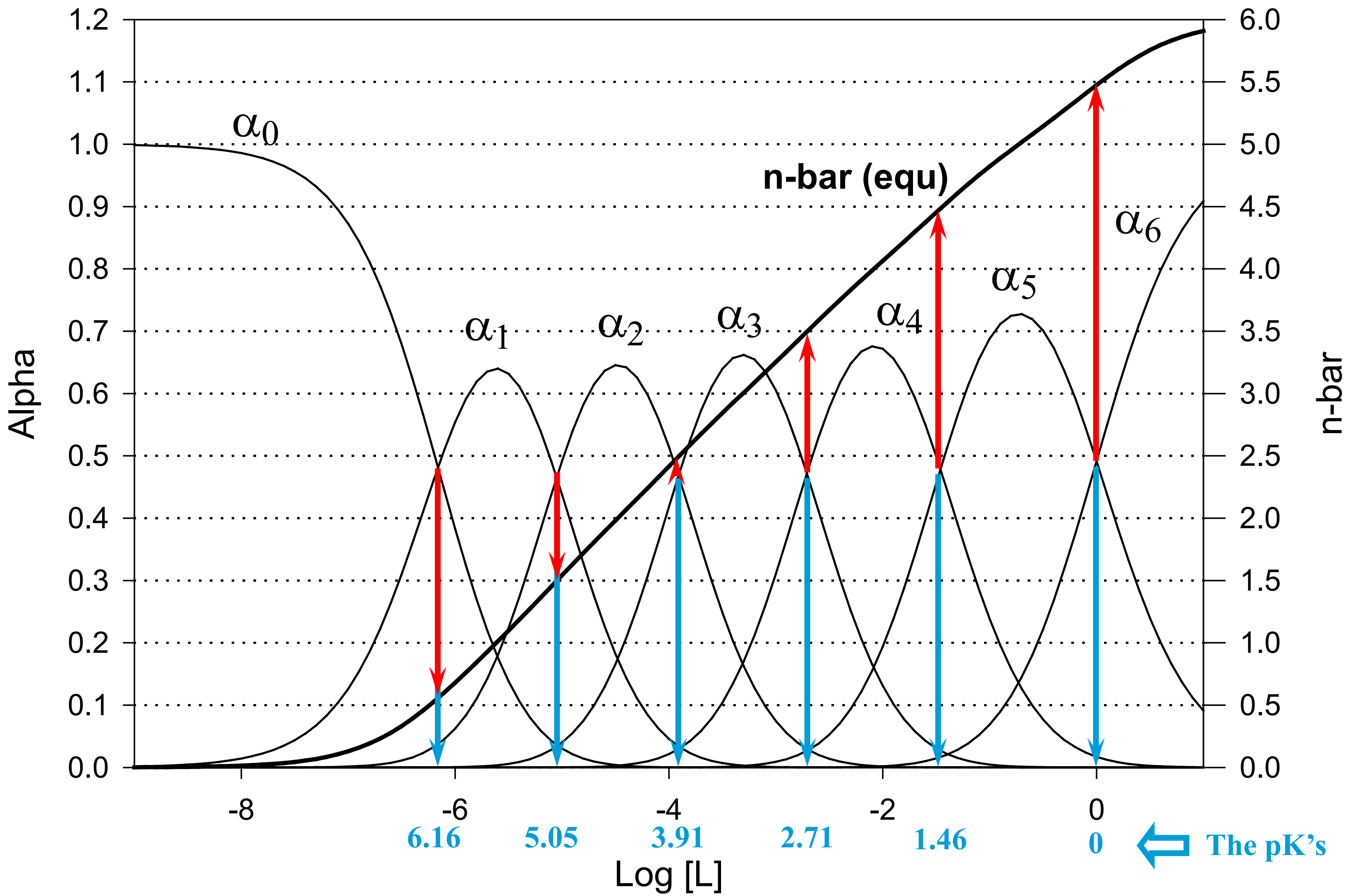
$$\alpha_n \equiv \frac{[ML_n]}{C_M} = \alpha_0 \beta_n [L]^n$$

Aluminum Fluoride



Aluminum Fluoride





Alpha
n-bar
n-bar (equ)
α0
α1
α2
α3
α4
α5
α6
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
-6
-4
-2
0
6.16
5.05
3.91
2.71
1.46
0
The pK's
Log [L]

Natural Fluoride

Figure 1.4, pg. 9 in Benjamin, 2015

$10^{-5.5}$ ⟺ $10^{-3.8}$

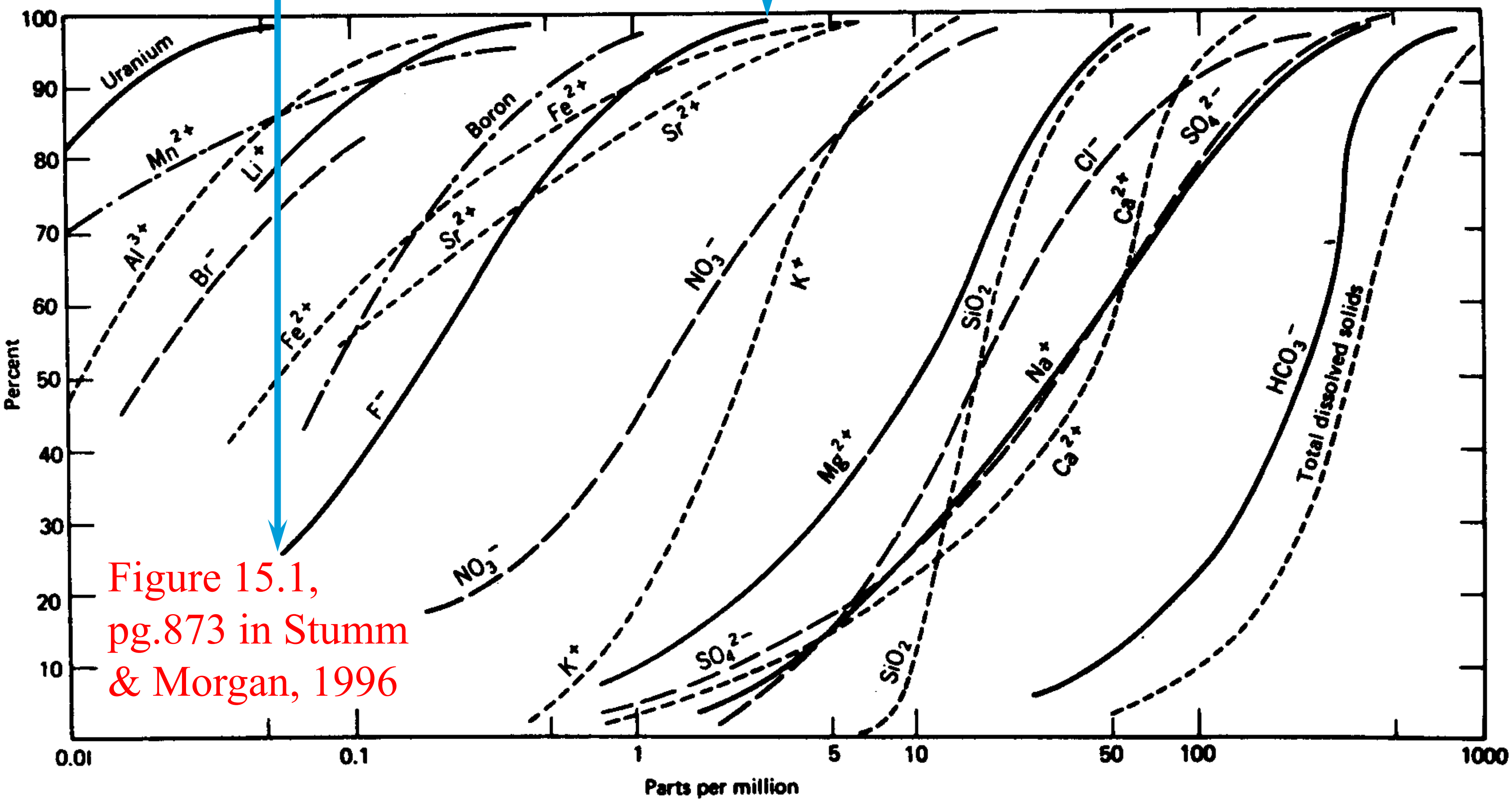
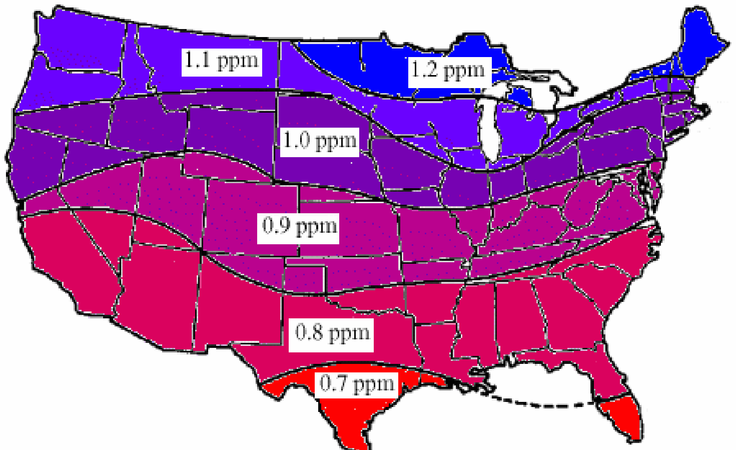


Figure 15.1, pg.873 in Stumm & Morgan, 1996

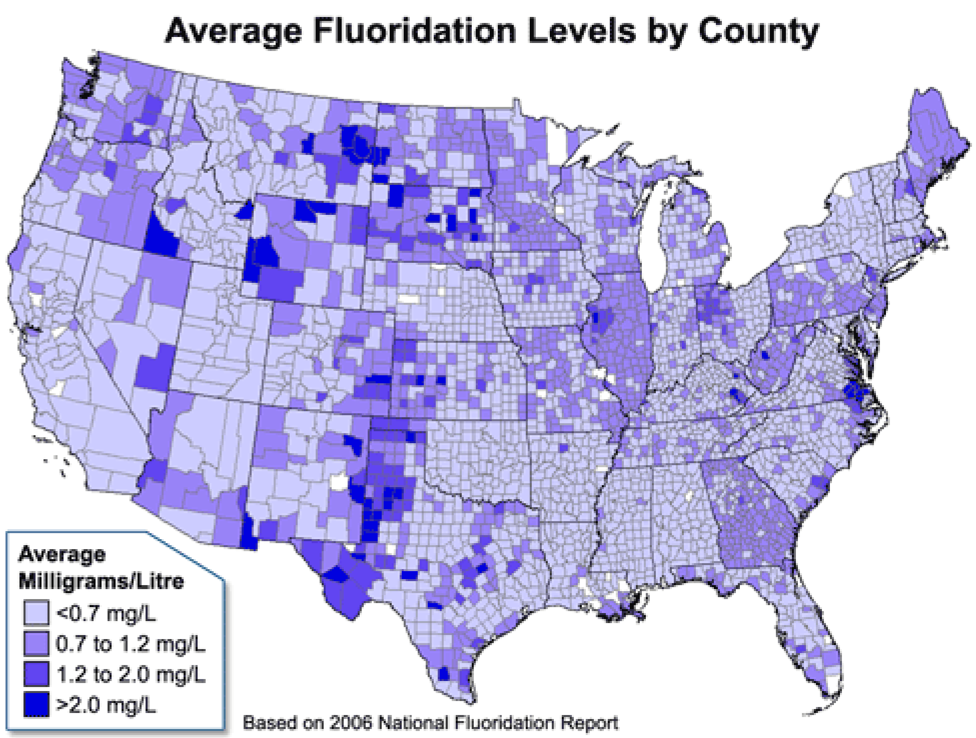
Fluoride addition

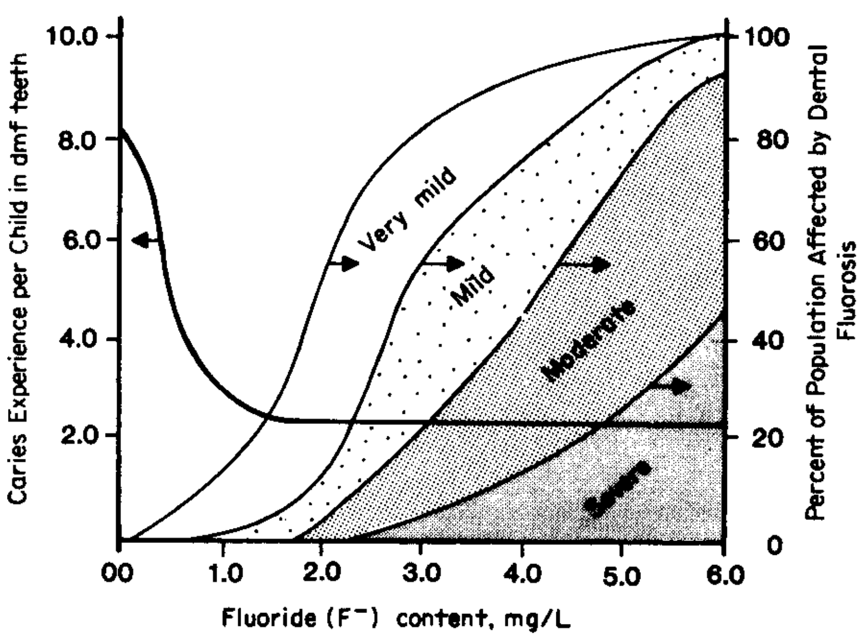
- Balance between Dental Caries and Fluorosis
- Recommended dose
  - 0.7 to 1.2 mg/L, Based on temperature



http://fluoride-math-tutorial.blogspot.com/

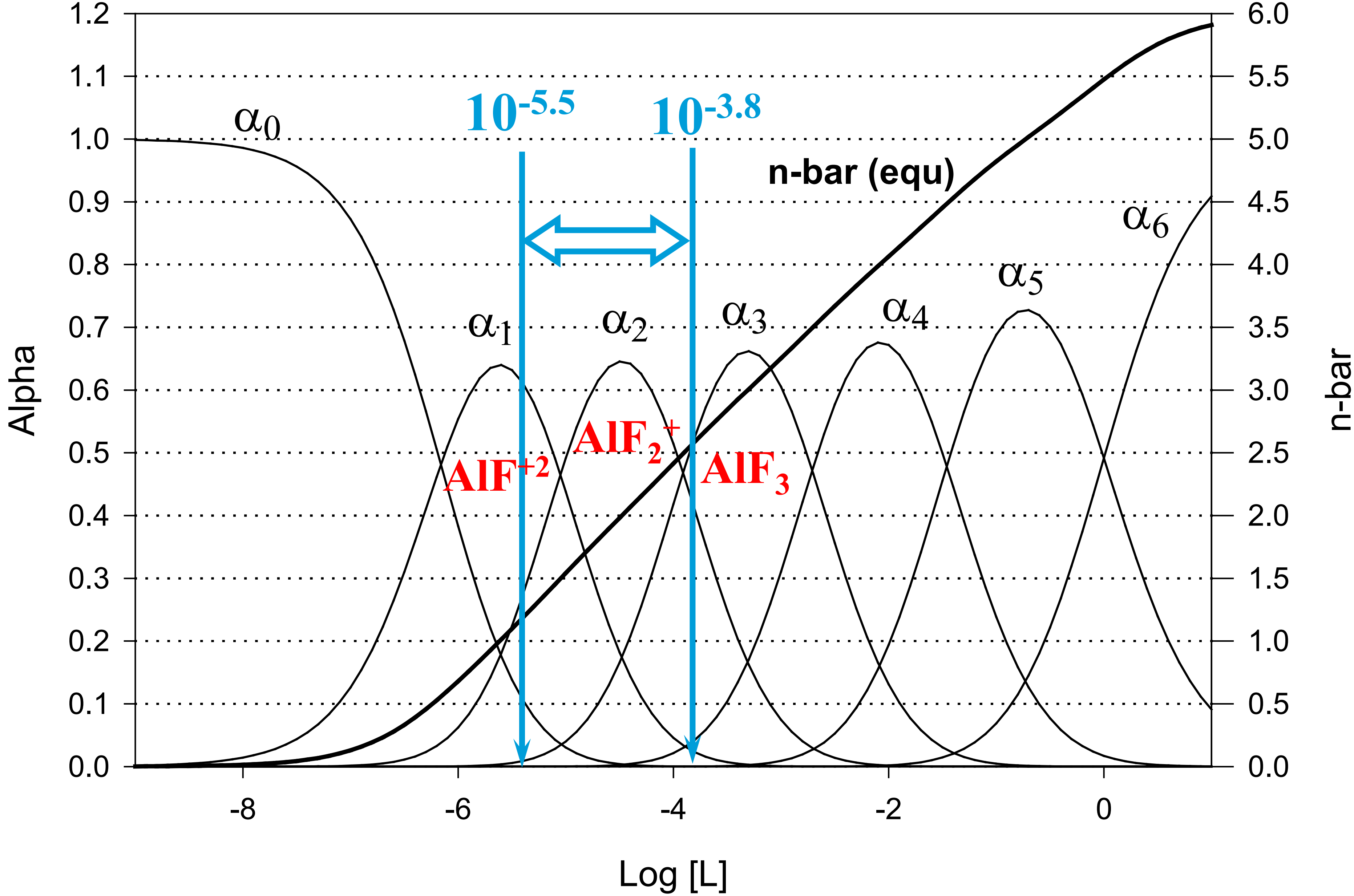
Fig. 15.3 from Water Quality & Treatment, 1999 (5th edition)





Al-F Problems & Discussion

- Typical WT Situation
  - Alum dose = 33 mg/L
  - Total Fluoride = 1.9 mg/L
- High Fluoride pulse & high alum dose
  - Alum dose = 660 mg/L
  - Total Fluoride = 190 mg/L
- Impacts of OH complexation?



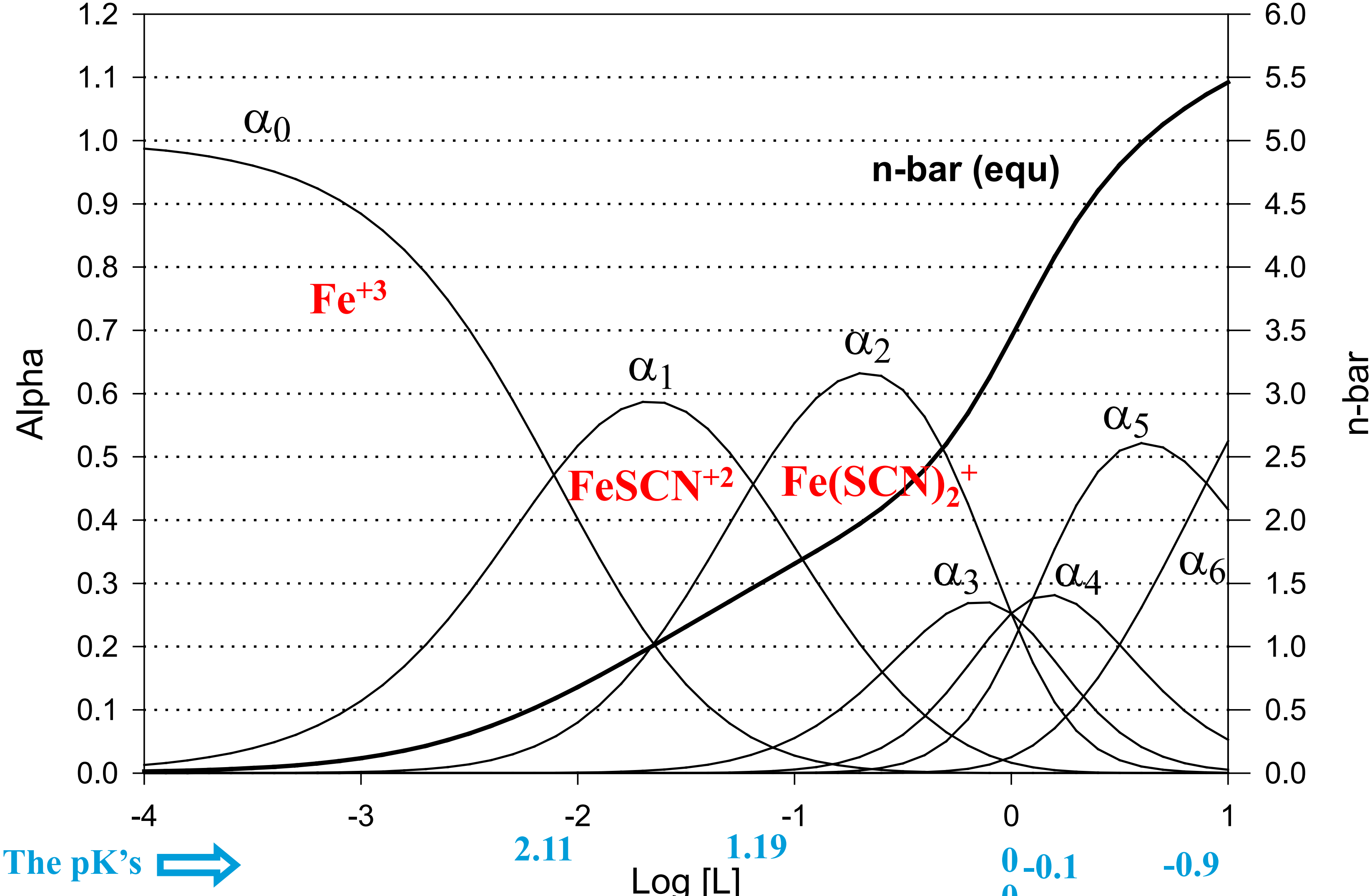
$10^{-5.5}$
$10^{-3.8}$
n-bar (equ)
α_0
α_1
α_2
α_3
α_4
α_5
α_6
AlF^{+2}
AlF_2^+
AlF_3
Alpha
n-bar
Log [L]
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-8
-6
-4
-2
0

Iron Thiocyanate system

- Significance
  - Metal plating wastewaters
  - Used in colorimetric analysis of iron
- Thermodynamic Values
  - Log K_1 = 2.11
  - Log K_2 = 1.19
  - Log K_3 = 0
  - Log K_4 = 0
  - Log K_5 = -0.1
  - Log K_6 = -0.9
- Now calculate alpha's

$$\alpha_0 \equiv \frac{[M]}{C_M} = \left(1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n\right)^{-1}$$

$$\alpha_n \equiv \frac{[ML_n]}{C_M} = \alpha_0 \beta_n [L]^n$$



The pK's ⇨ 2.11 1.19 0 0 -0.1 -0.9

Specific problem

- Total concentrations
  - C_M = 0.1 M
  - C_L = 0.1 M
- Mass based equation
  - N-bar = 1-10[SCN^-]
- Solution: n-bar = 0.85
  - [Fe^{+3}]=0.028M
  - [$FeSCN^{+2}$] = 0.057M
  - [$Fe(SCN)_2^+$] = 0.014M

Fe-S problem

- 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. Prepare a 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.

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

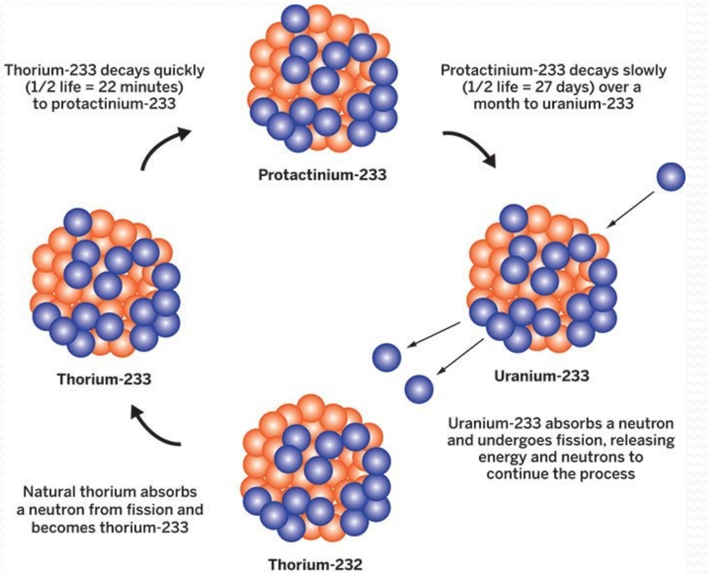
Log ß values (From Table 8.3 ; pg 374)

Thorium

- ^{232}Th is 99.98% of natural abundance
  - weakly radioactive ($t_{1/2}$ = 14 billion yrs)
  - Most abundant radioactive element in nature
- Uses:
  - Nuclear power: forms ^{233}U
    - $^{232}_{90}Th + n \rightarrow ^{233}_{90}Th + \gamma \rightarrow ^{233}_{91}Pa \rightarrow ^{233}_{92}U$
- Health effects:
  - Bone, liver and lung cancer
- Solvated by 9 waters (like many Lanthanide and Actinide elements

No specific standard, but EPA has established a Maximum Contaminant Level (MCL) of 15 picoCuries per liter (pCi/L) for alpha particle activity, excluding radon and uranium, in drinking water.

1 Ci = 3.7x10^{10} dps

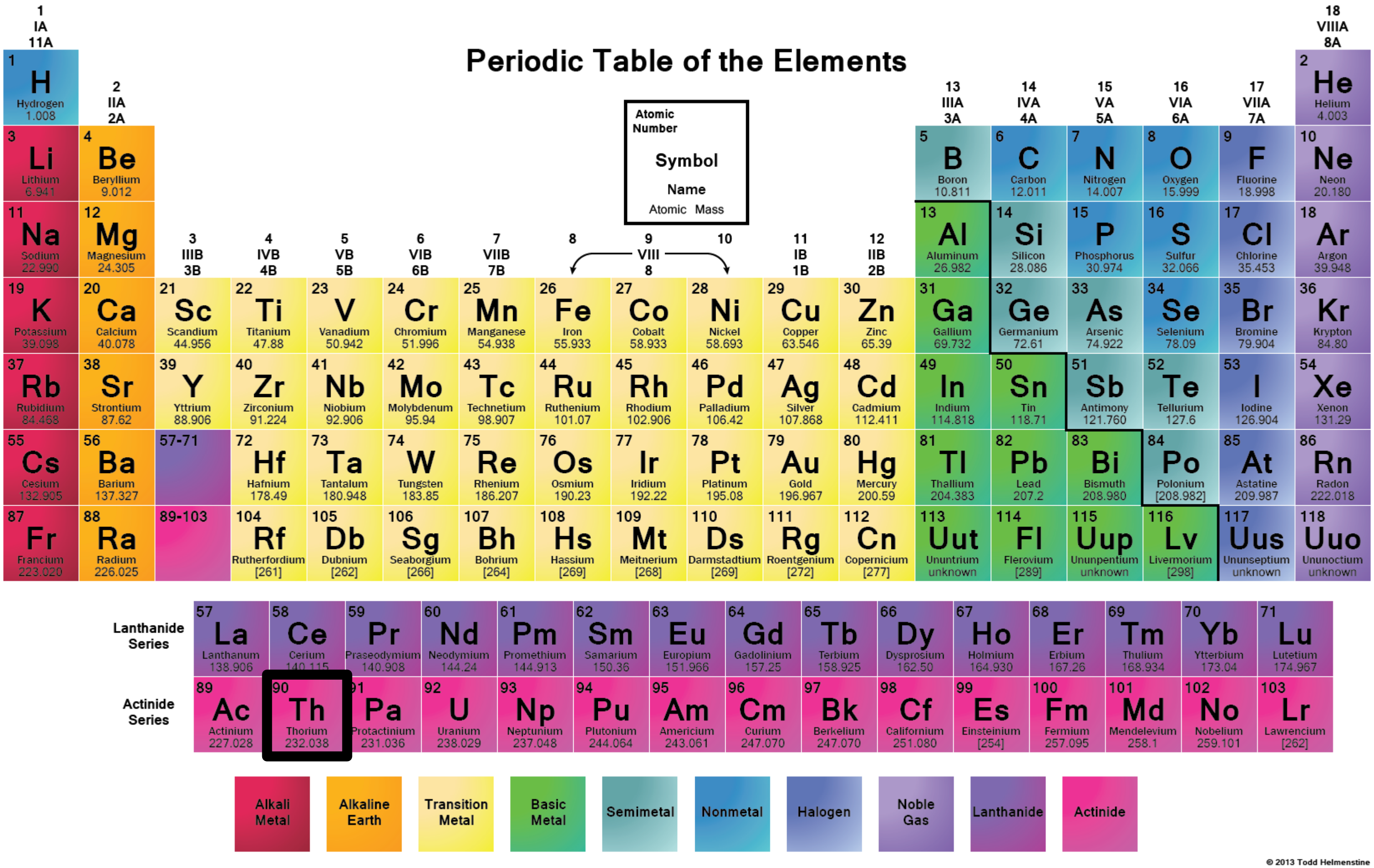


Converting pCi/L to ug/L

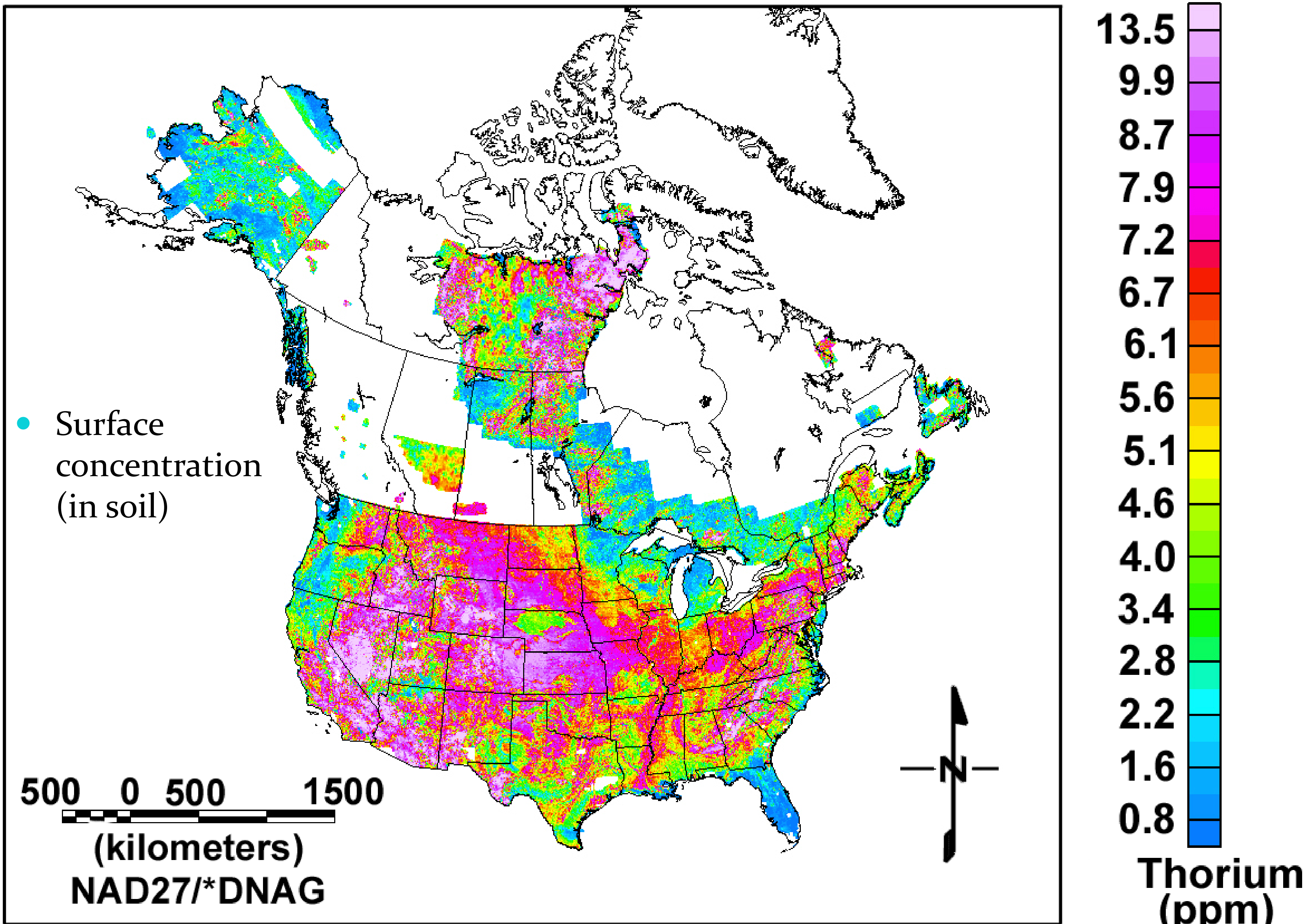
- Spreadsheet calculation for Thorium-232

Thorium	232	AMU										
		EPA MCL	15	pCi/L =	1.5E-11	Ci/L			1	Ci =	3.7E+10	d/s
					0.555	d/s/L						
		Th 232										
			t 1/2 =	14000000000	years							
			k =	4.95105E-11	per year					Avogadro's #	6.02E+23	atoms/mole
			disintegration rate=	2.98053E+13	d/mole/yr =	944473.9	d/mole/s					
			conc =	5.87629E-07	moles/L =	0.587629	uM =	136	ug/L			

Thorium: Actinide Element



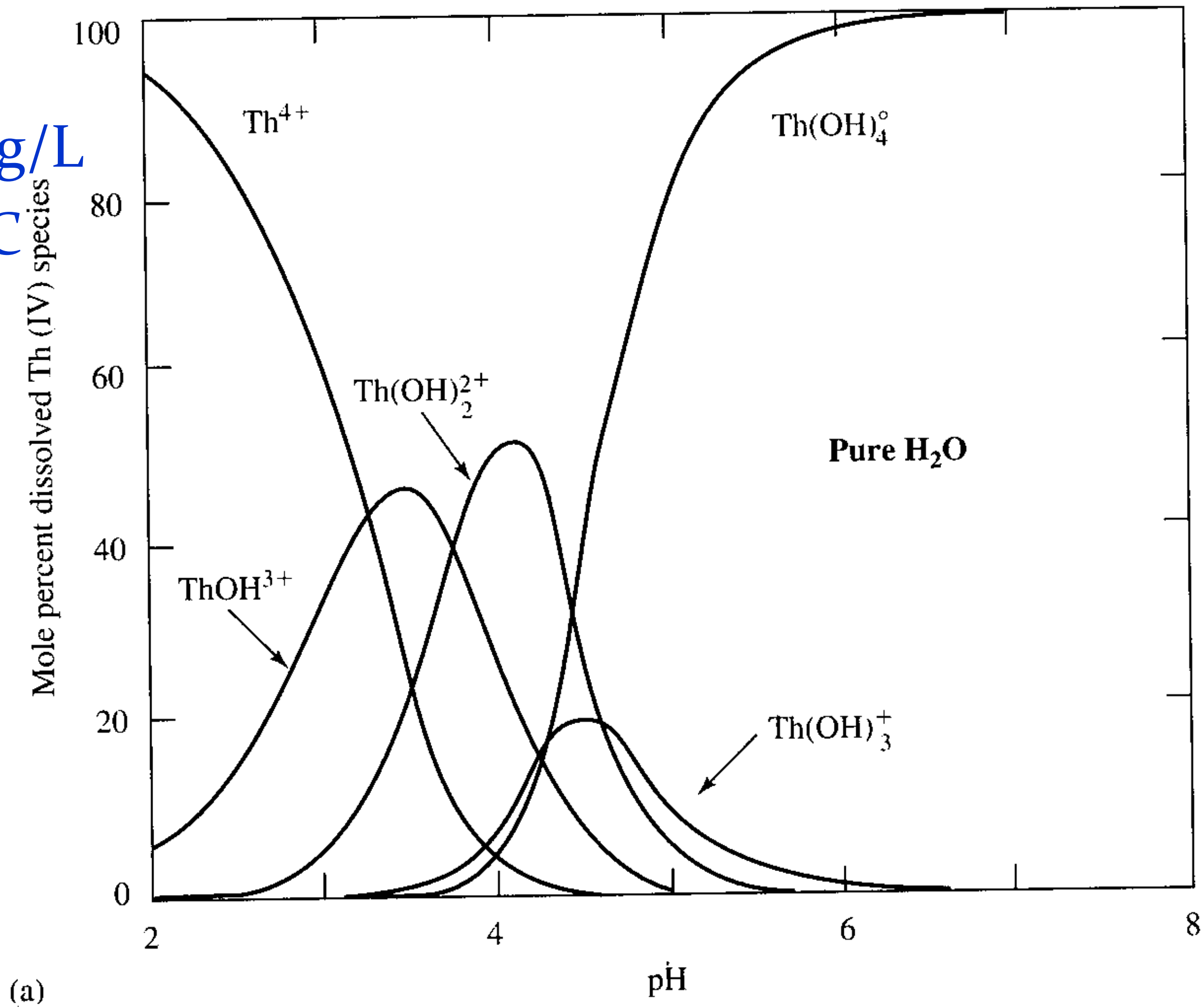
Thorium Concentrations



- Surface concentration (in soil)

Thorium example I

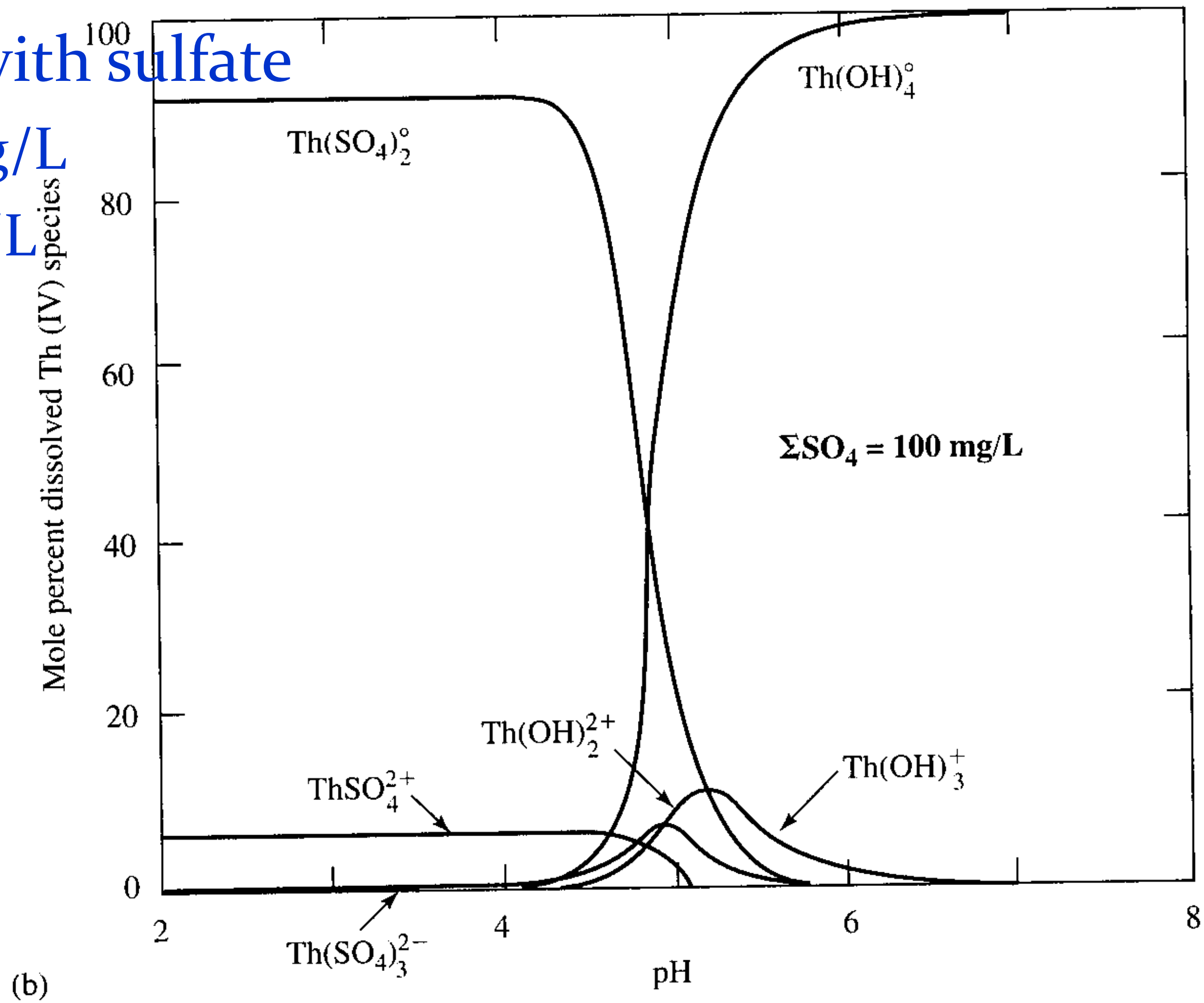
- In pure water
  - C_{Th} = 0.01 µg/L
  - Temp = 25ºC



From: Langmuir, 1997; Fig. 3.12a,
Original source: Langmuir & Herman, 1980; *Geochim. Et Cosmochim. Acta* 44(11)1753-1766

Thorium example II

- In pure water with sulfate
  - C_{SO_4} = 100 mg/L
  - C_{Th} = 0.01 µg/L
  - Temp = 25ºC



From: Langmuir, 1997, Fig. 3.12b

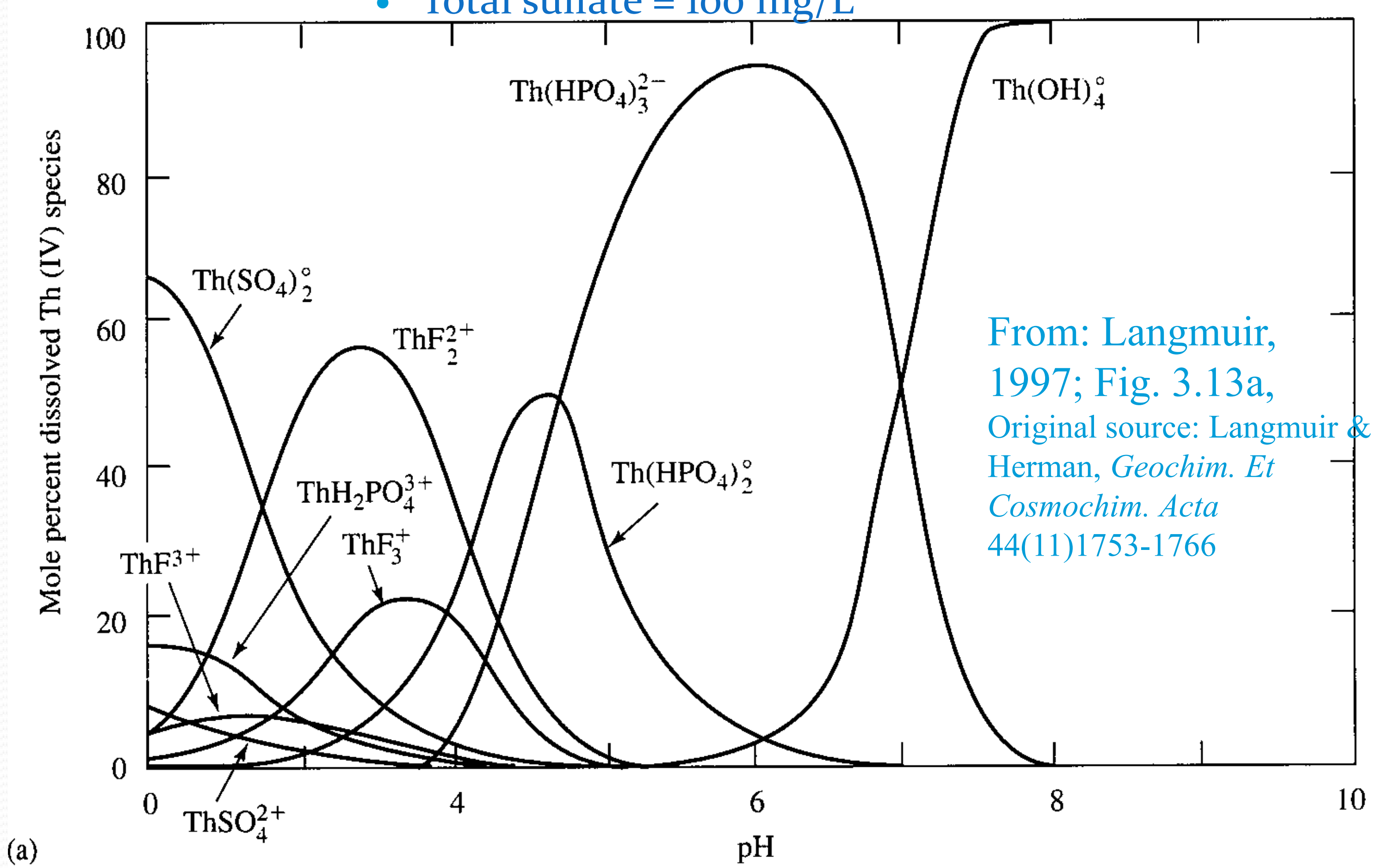
Original source: Langmuir & Herman, 1980; *Geochim. Et Cosmochim. Acta* 44(11)1753-1766

Thorium example III

- Model groundwater without organics
  - C_{Th} = 0.01 µg/L & Temp = 25ºC
  - Groundwater composition
    - Total fluoride = 0.3 mg/L
    - Total chloride = 10 mg/L
    - Total phosphate = 0.1 mg/L
    - Total sulfate = 100 mg/L

Up to 220 mg-Th/kg-P in phosphate rock, less in P from sewage sludge

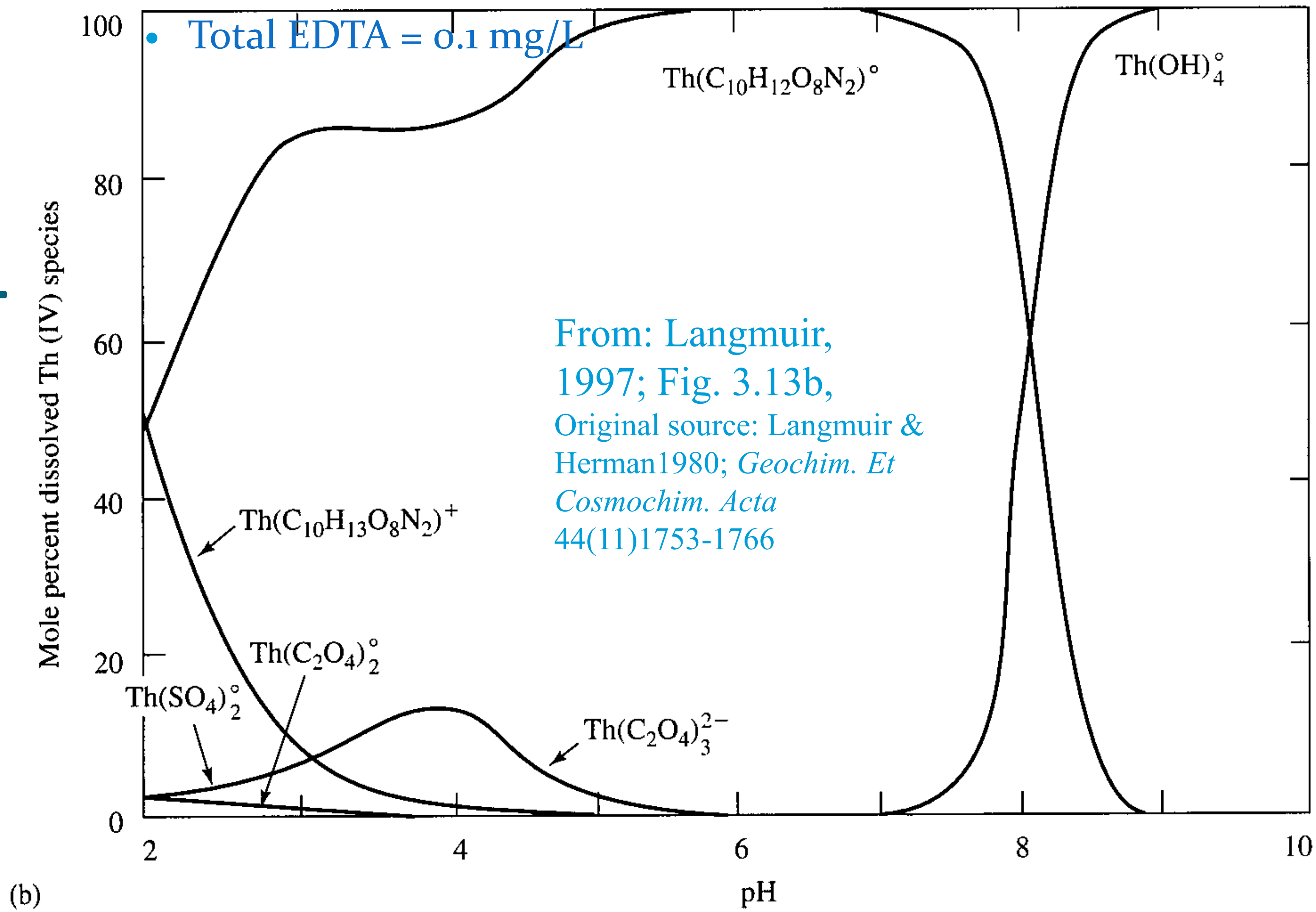
Th-P solids are less bioavailable



From: Langmuir, 1997; Fig. 3.13a, Original source: Langmuir & Herman, *Geochim. Et Cosmochim. Acta* 44(11)1753-1766

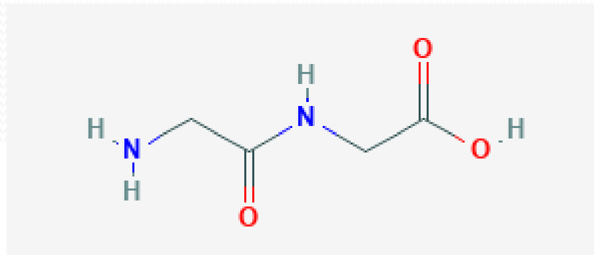
Thorium example IV

- Model groundwater with organics
  - Same inorganic groundwater composition
  - With organics
    - Total oxalate = 1.0 mg/L
    - Total EDTA = 0.1 mg/L

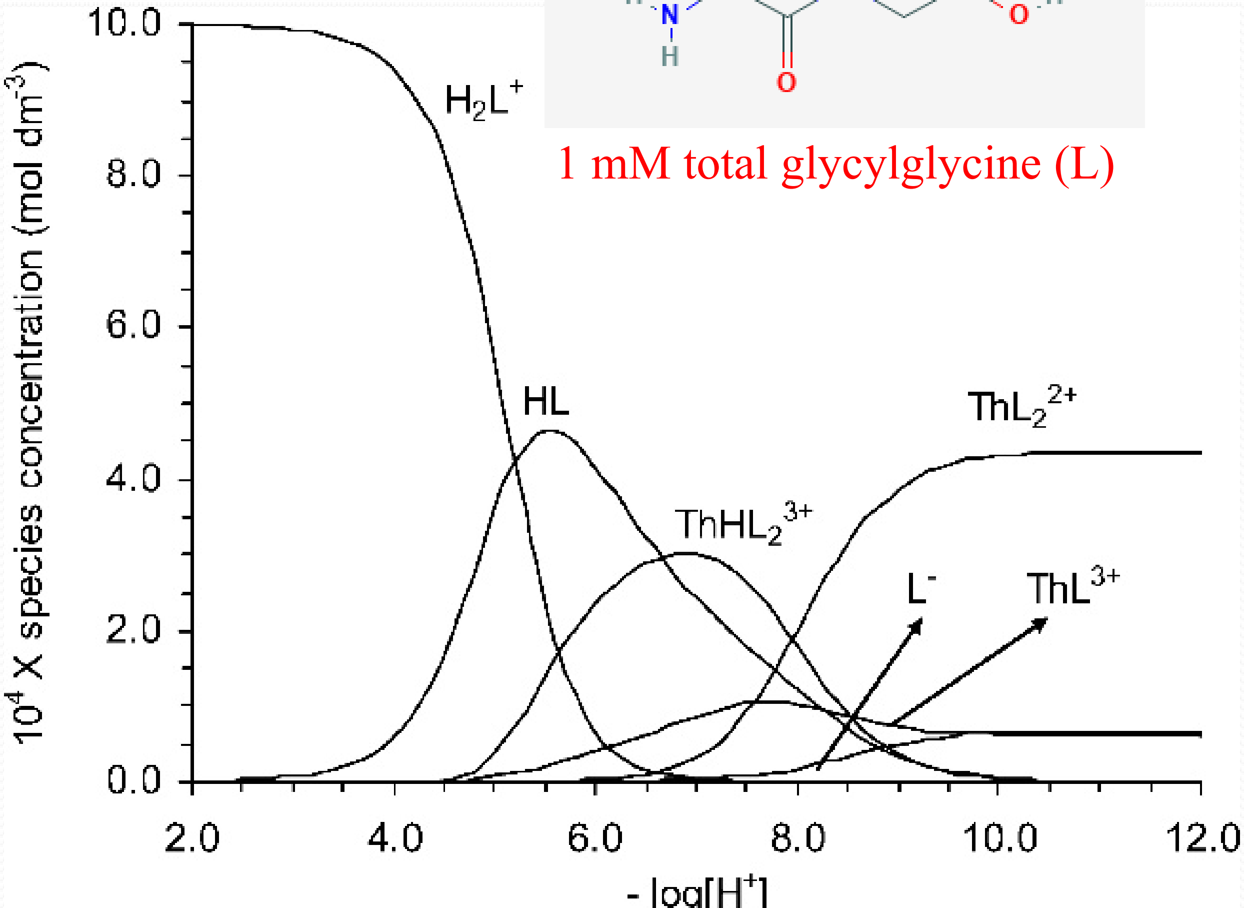


From: Langmuir, 1997; Fig. 3.13b,
Original source: Langmuir & Herman1980; *Geochim. Et Cosmochim. Acta* 44(11)1753-1766

In the human body



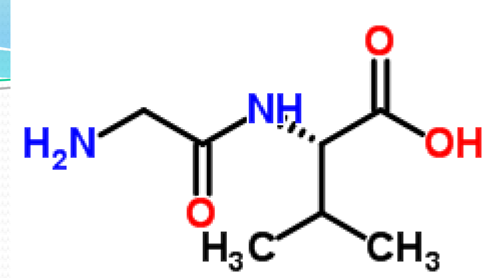
1 mM total glycylglycine (L)



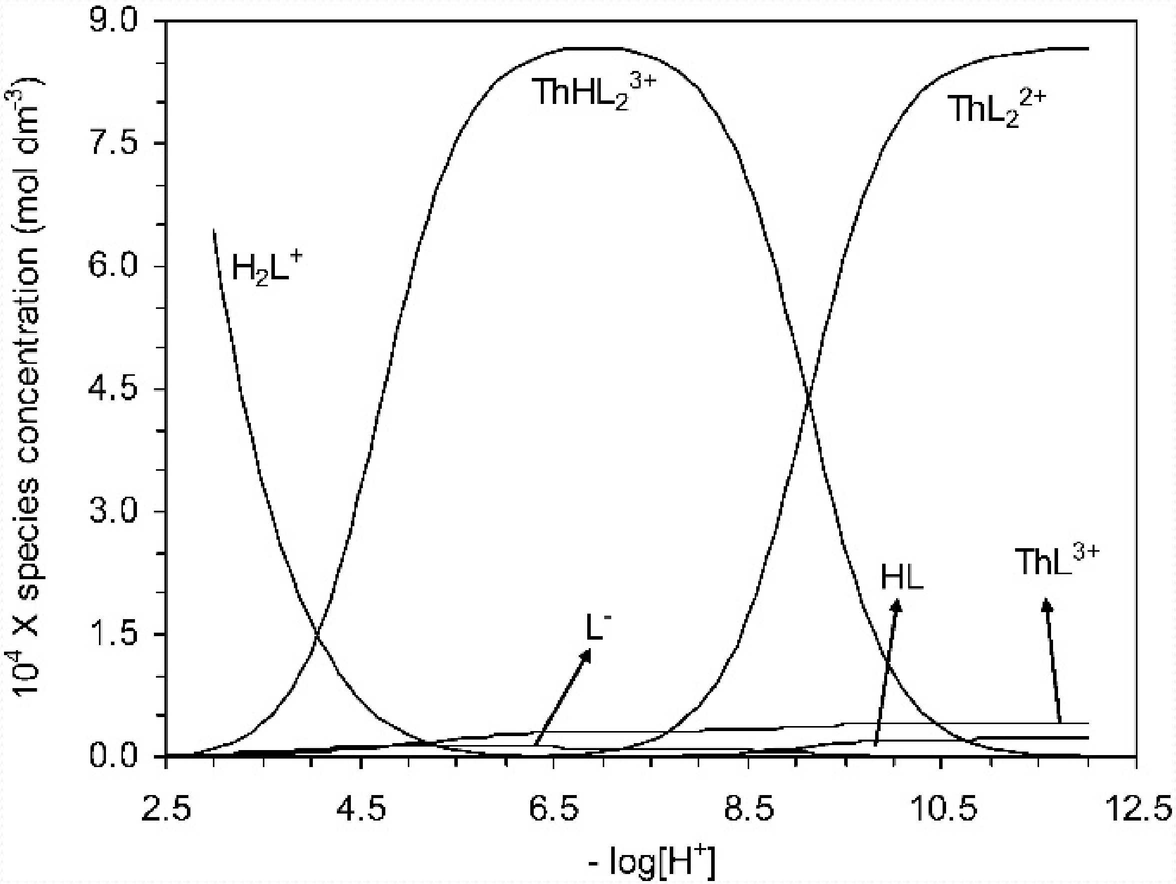
- "The thorium(IV) ion readily reacts with in vivo amino acids, peptides, nucleic acids, proteins, etc. to form stable complexes which are distributed in the body, primarily in the liver, bone, and kidneys"

Kiani et al., 2009 J. Chem. Eng. Data, 54(12) 3247-3251, "Complex Formation of Thorium(IV) Ion with Glycyl-Glycine and Glycyl-Valine"

Another dipeptide



- This time with 1 mM total glycylvaline (L)



Kiani et al., 2009 J. Chem. Eng. Data, 54(12) 3247-3251, "Complex Formation of Thorium(IV) Ion with Glycyl-Glycine and Glycyl-Valine"

End

- To next lecture

Fe-S problem

- 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. Prepare a 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.

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

Log ß values (From Table 8.3 ; pg 374)

Calculations

Log ß values (From Table 8.3 ; pg 374)

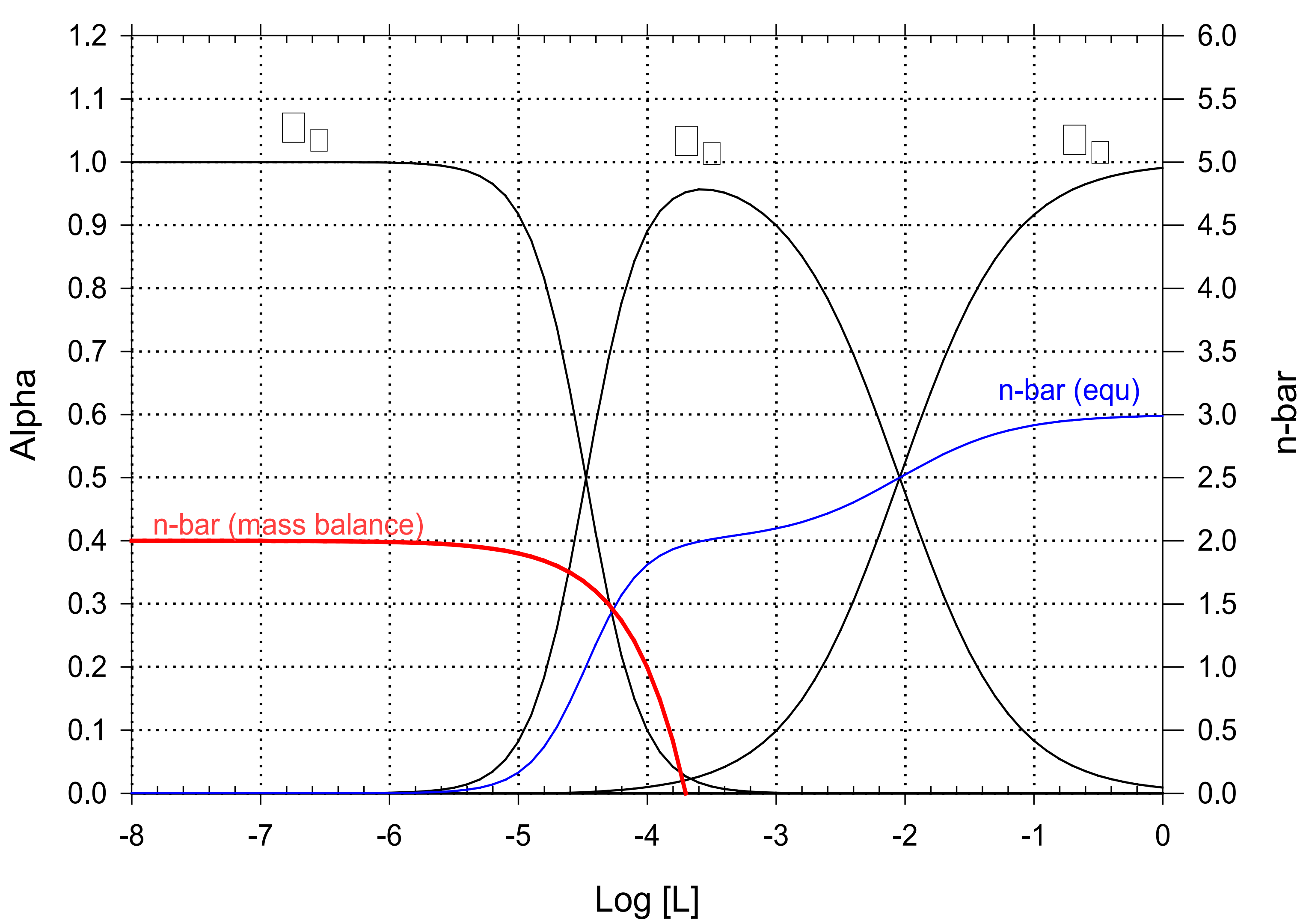
Species	Ligand	
	HS-	PO_4^{-3}
FeL_2	8.95	
FeL_3	10.99	
FeH_2L		22.25

- calculations

$$\beta_2 = 10^{8.95} = \frac{[FeL_2]}{[Fe]\,[L^2]}$$

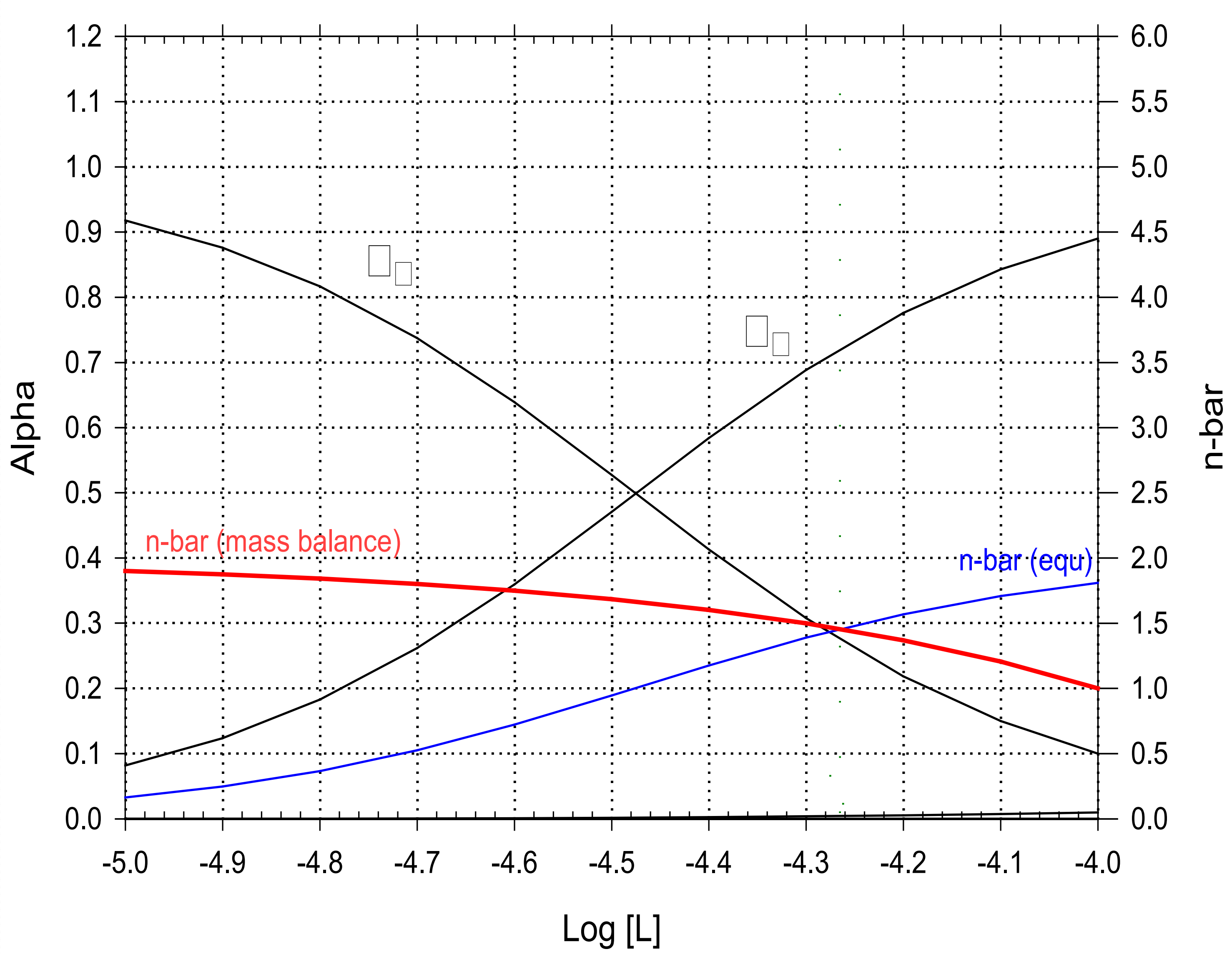
$$\beta_3 = 10^{10.99} = \frac{[FeL_3]}{[Fe]\,[L^3]}$$

- a



n-bar (mass balance)
n-bar (equ)
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
-8
-7
-6
-5
-4
-3
-2
-1
0

- a



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

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