

CEE 680: Water Chemistry

Lecture #30

Coordination Chemistry: case studies

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

Benjamin; Chapter 8.1-8.6

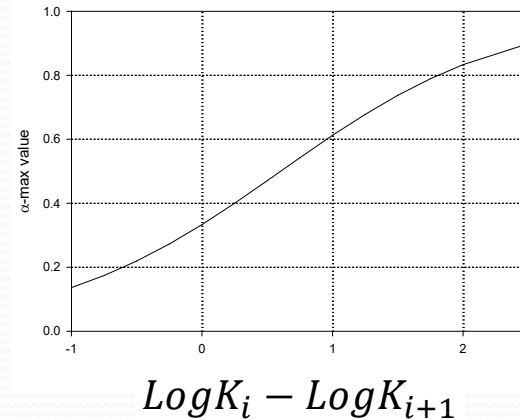
Summary of a few general rules

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

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

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

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



- 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

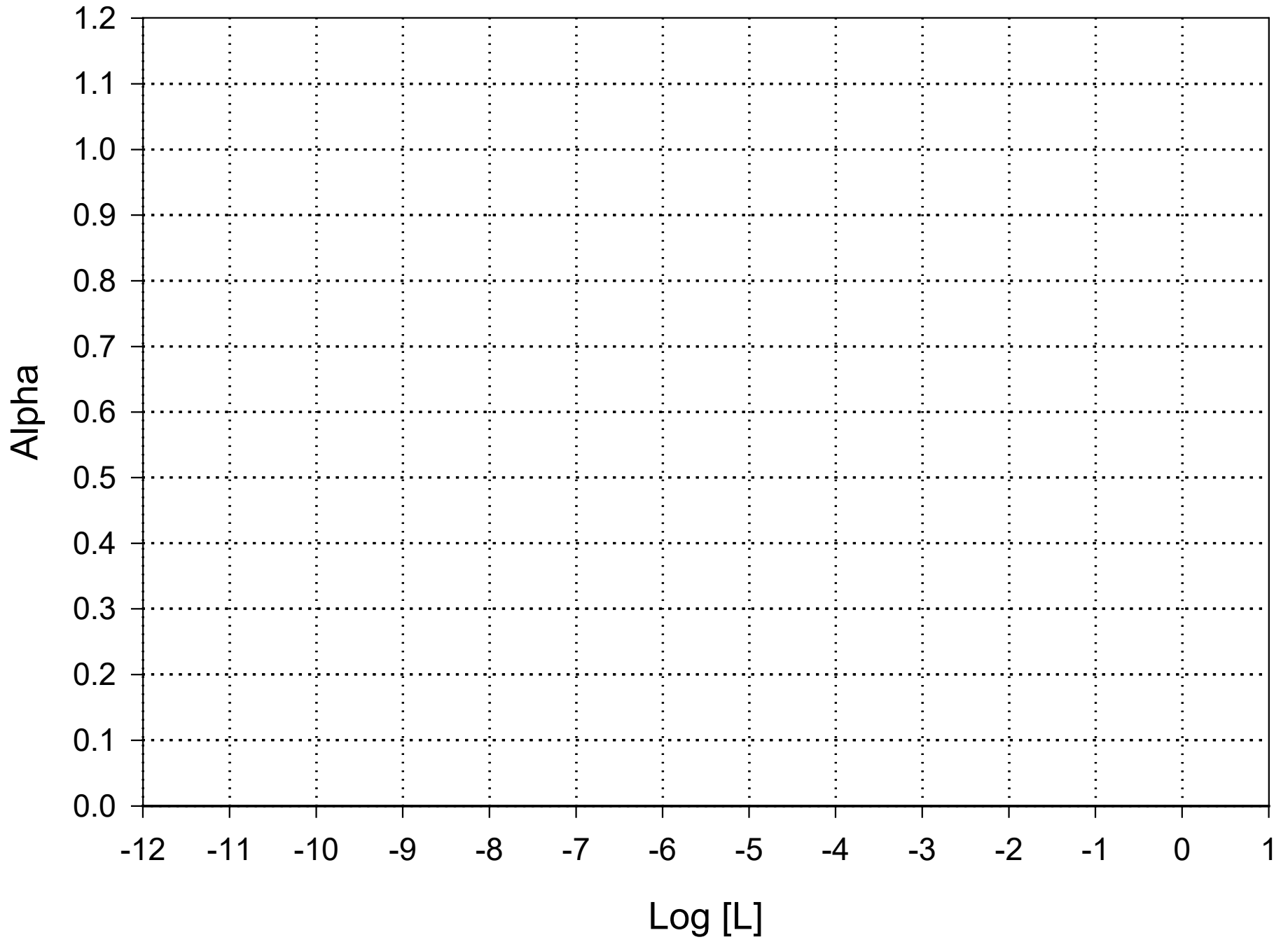
- Bisulfide Ligand

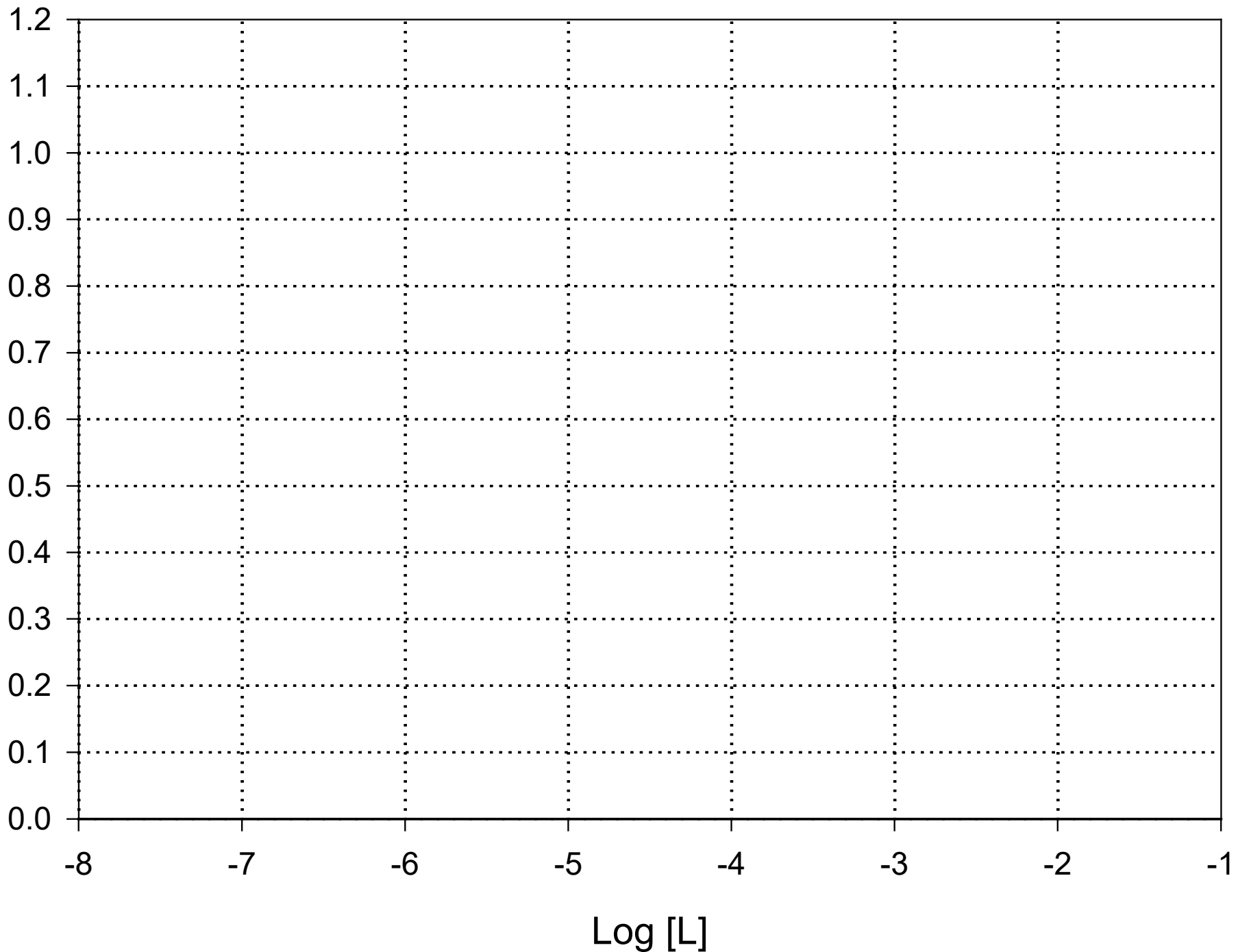
Species	log K	Log Beta
CdL	Log $K_1 = 10.17$	Log $\beta_1 = 10.17$
CdL ₂	Log $K_2 = 6.36$	Log $\beta_2 = 16.53$
CdL ₃	Log $K_3 = 2.18$	Log $\beta_3 = 18.71$
CdL ₄	Log $K_4 = 2.19$	Log $\beta_4 = 20.90$

- Cyanide Ligand

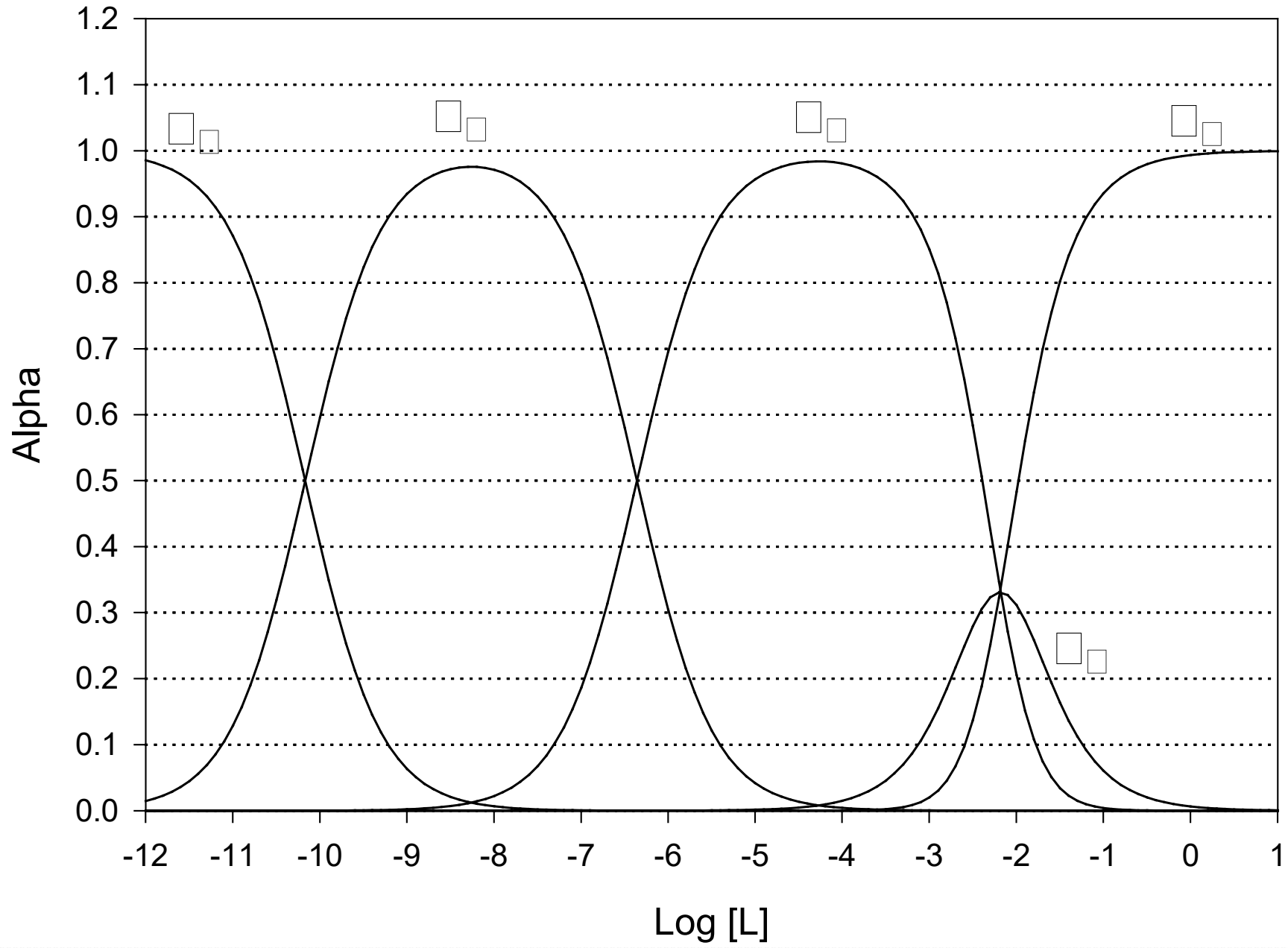
Species	log K	Log Beta
CdL	Log $K_1 = 5.32$	Log $\beta_1 = 5.32$
CdL ₂	Log $K_2 = 5.05$	Log $\beta_2 = 10.37$
CdL ₃	Log $K_3 = 4.46$	Log $\beta_3 = 14.83$
CdL ₄	Log $K_4 = 3.46$	Log $\beta_4 = 18.29$

Cd-HS system





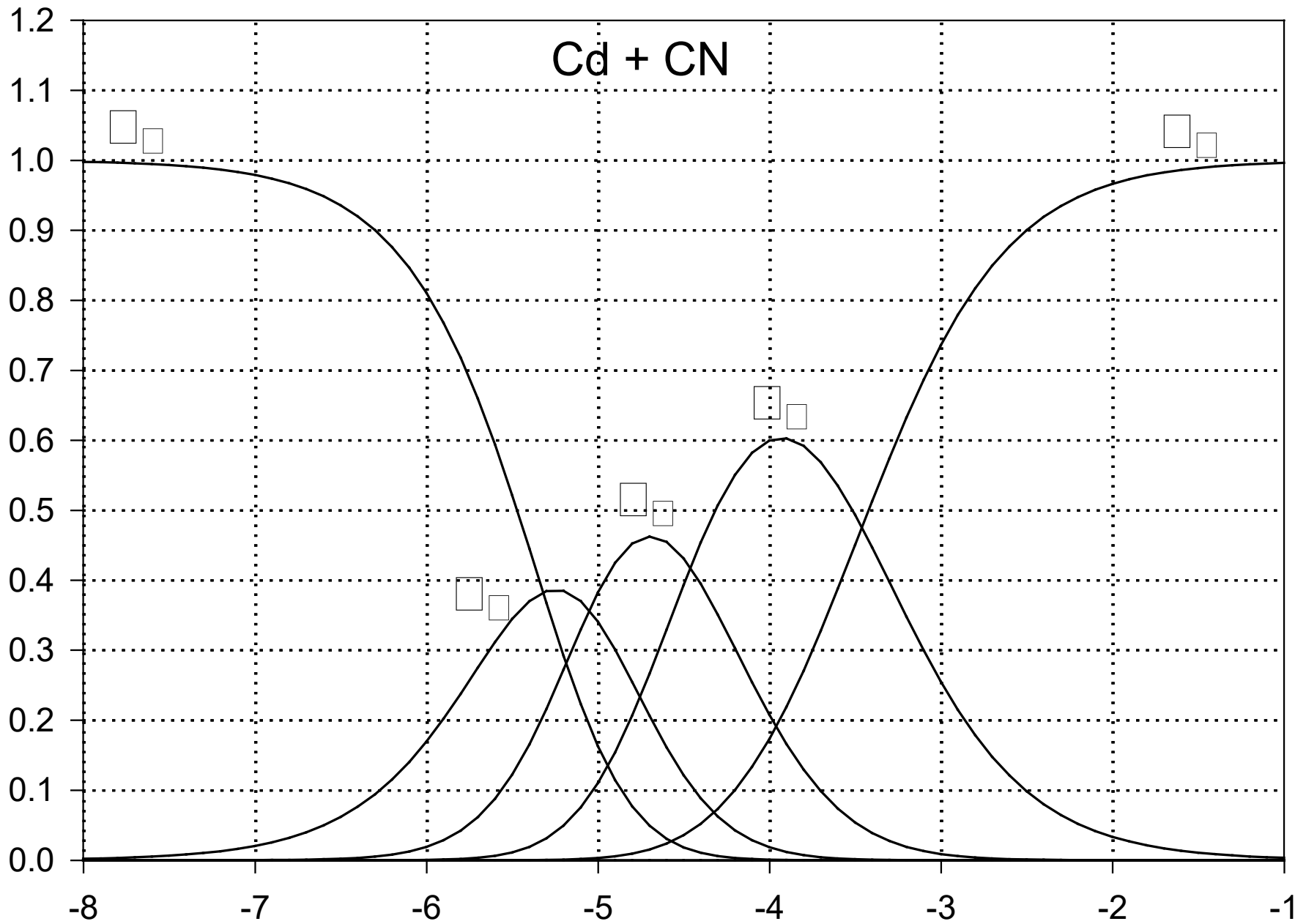
Cd-HS system



Cd + CN

Alpha

Log [L]

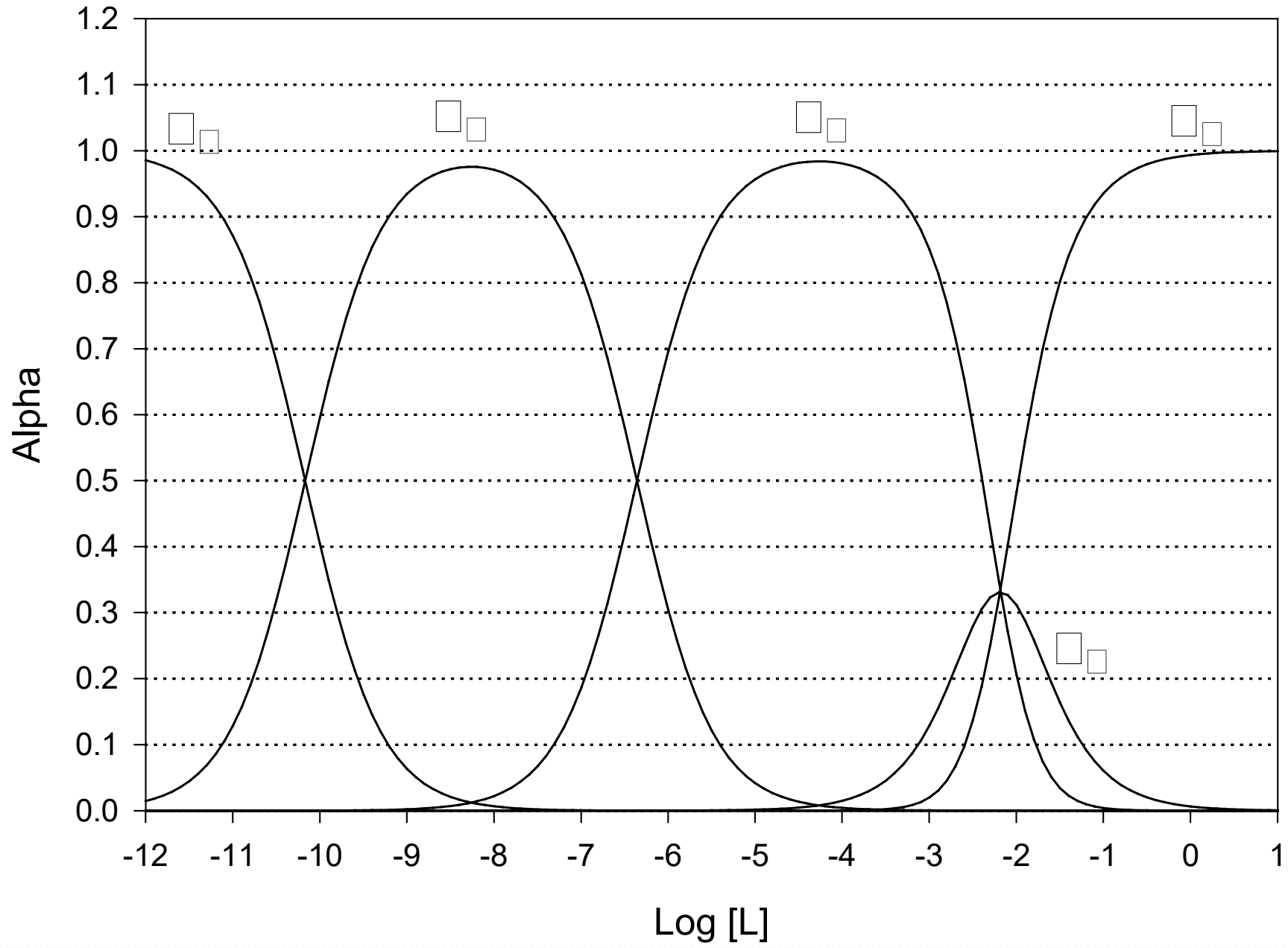


Cadmium Bisulfide

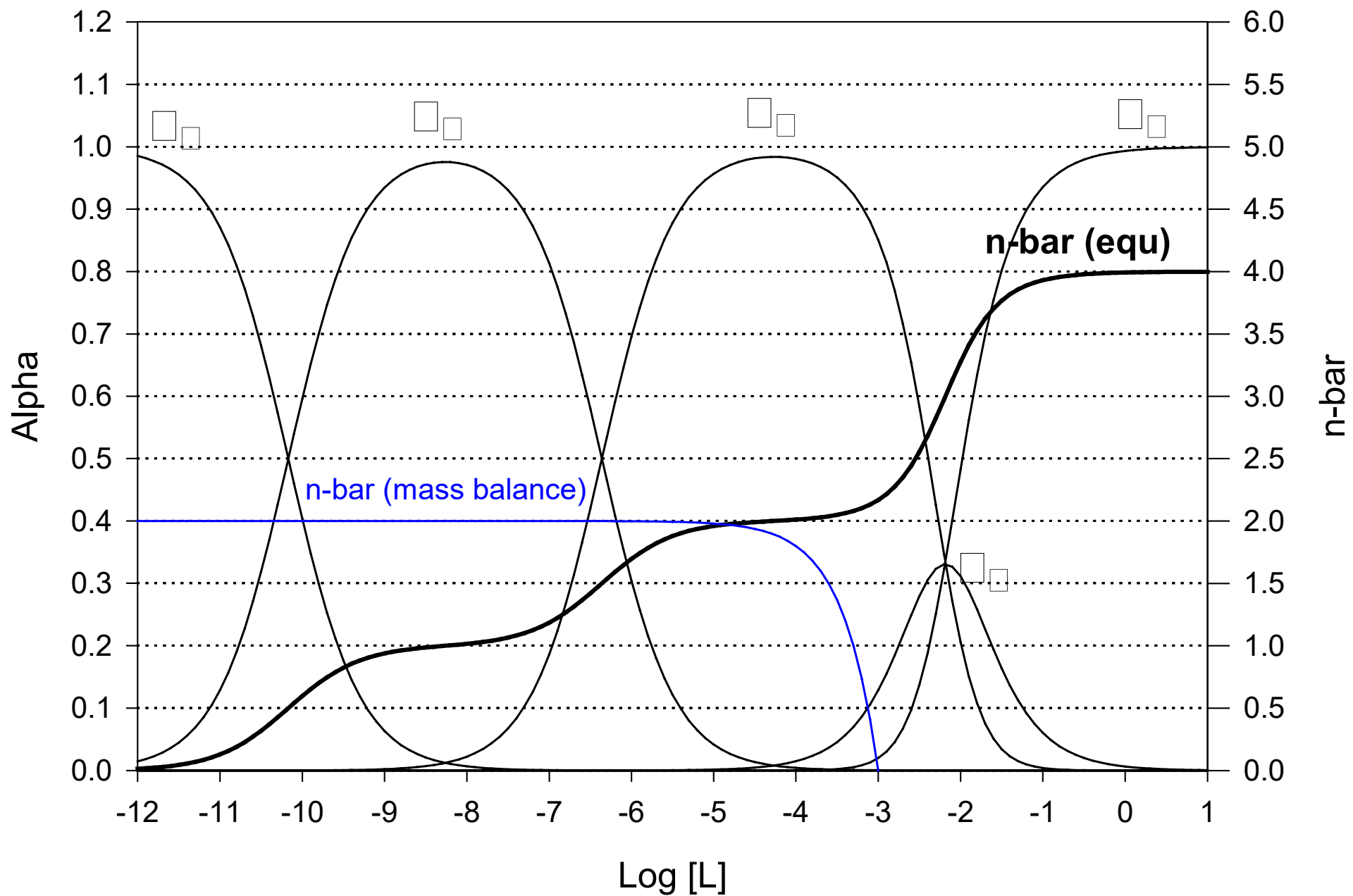
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CdL ₃	Log $K_3 = 2.18$	Log $\beta_3 = 18.71$
CdL ₄	Log $K_4 = 2.19$	Log $\beta_4 = 20.90$

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

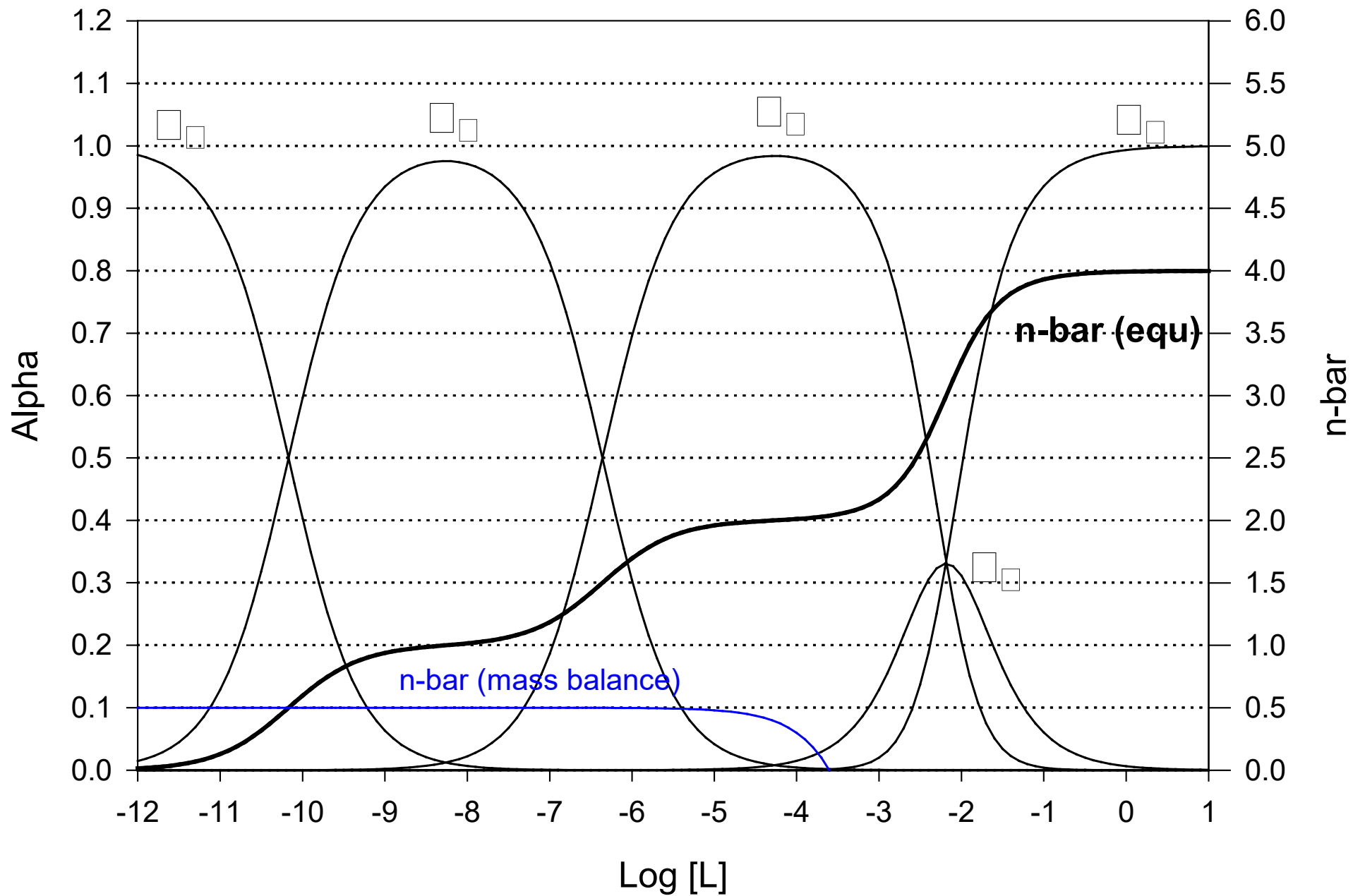
Cd-HS system



$5 \times 10^{-4} \text{ M Cd}_{\text{Total}} + 10^{-3} \text{ M HS}_{\text{Total}}$



$1 \times 10^{-3} \text{M Cd}_{\text{Total}} + 5 \times 10^{-4} \text{M HS}_{\text{Total}}$



Cadmium Cyanide

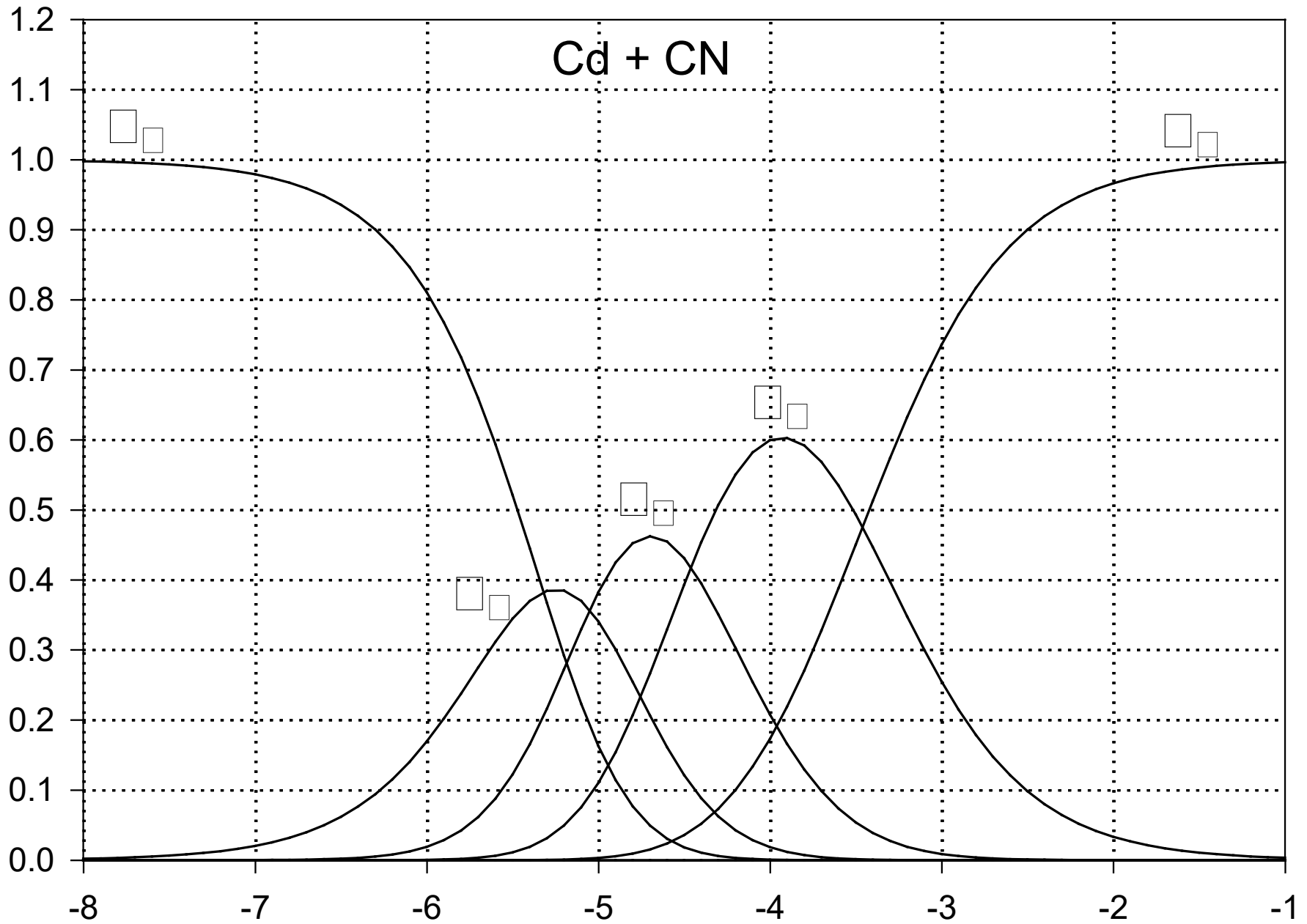
Species	log K	Log Beta
CdL	Log $K_1 = 5.32$	Log $\beta_1 = 5.32$
CdL ₂	Log $K_2 = 5.05$	Log $\beta_2 = 10.37$
CdL ₃	Log $K_3 = 4.46$	Log $\beta_3 = 14.83$
CdL ₄	Log $K_4 = 3.46$	Log $\beta_4 = 18.29$

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

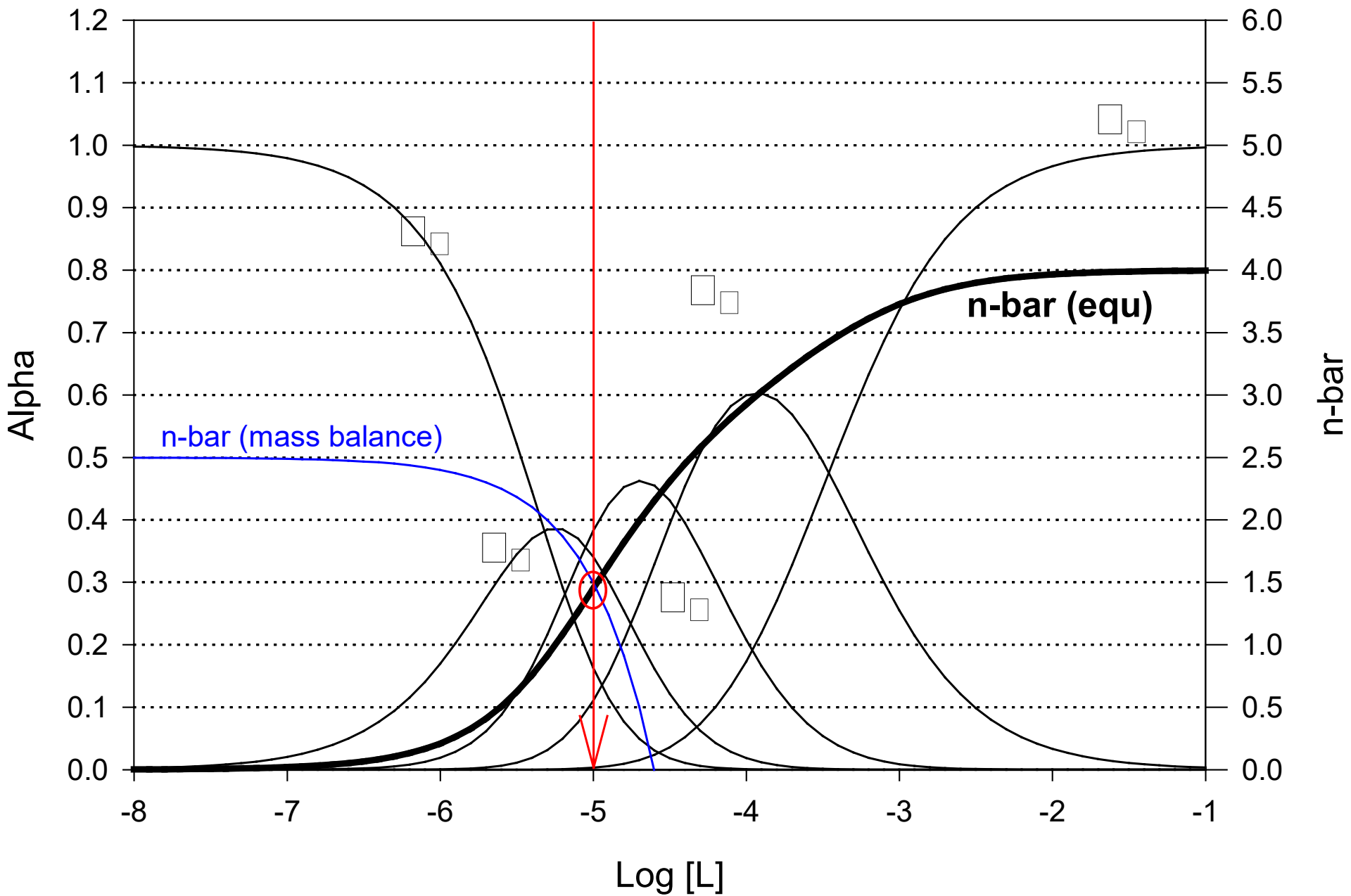
Cd + CN

Alpha

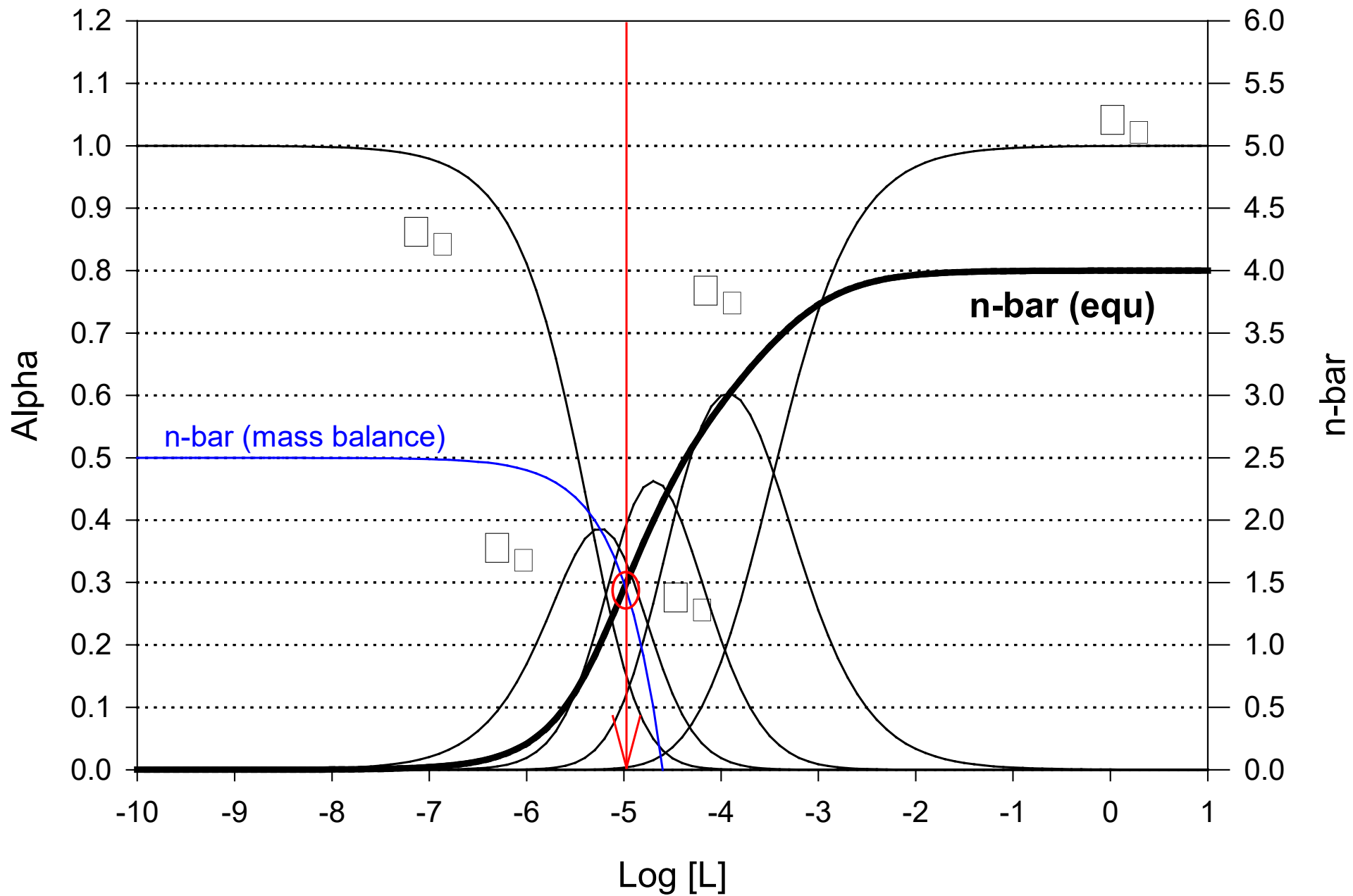
Log [L]



$10^{-5} \text{M Cd}_{\text{Total}} + 2.5 \times 10^{-5} \text{M CN}_{\text{Total}}$



$10^{-5} \text{M Cd}_{\text{Total}} + 2.5 \times 10^{-5} \text{M CN}_{\text{Total}}$

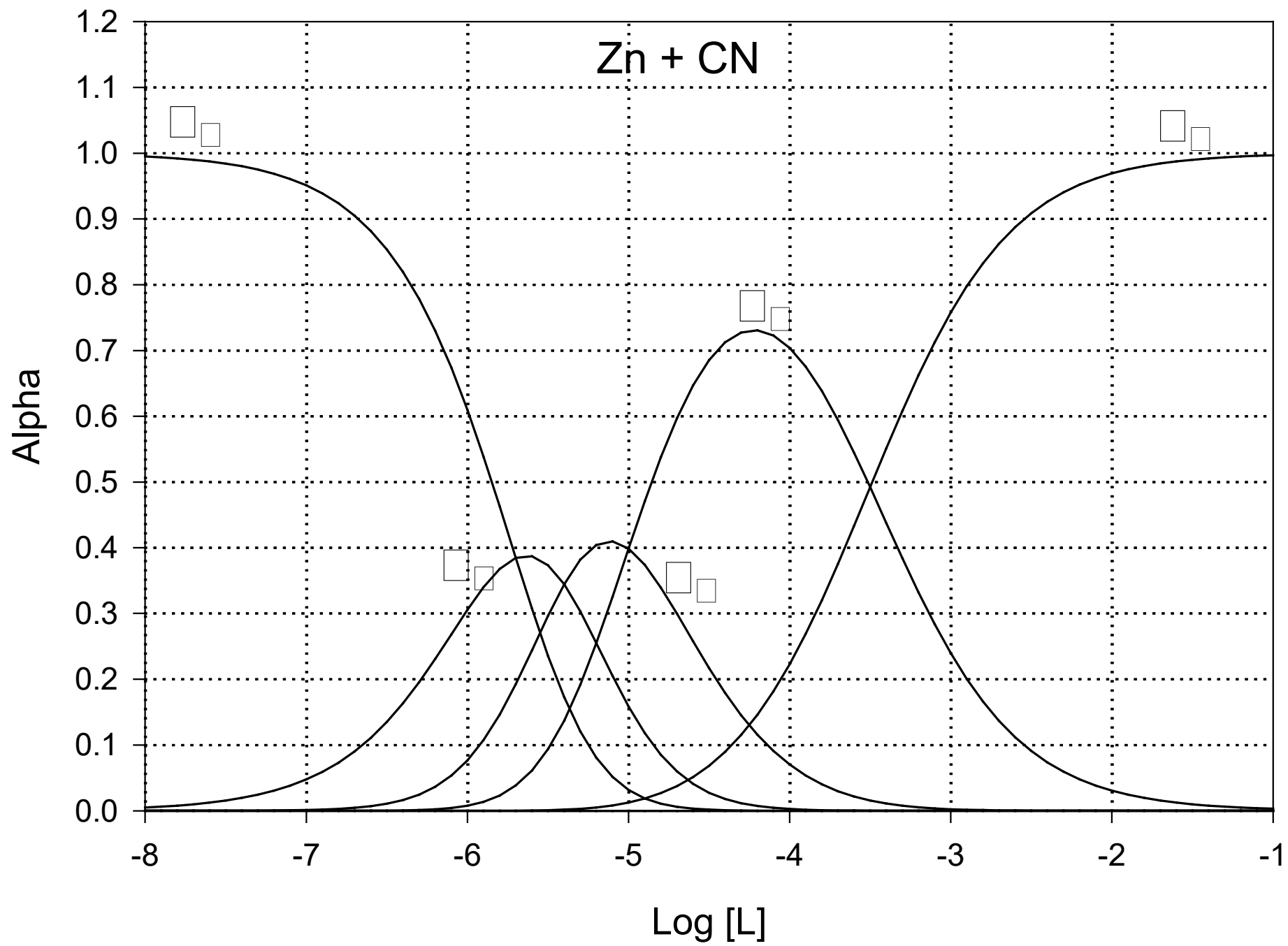


Zinc Cyanide

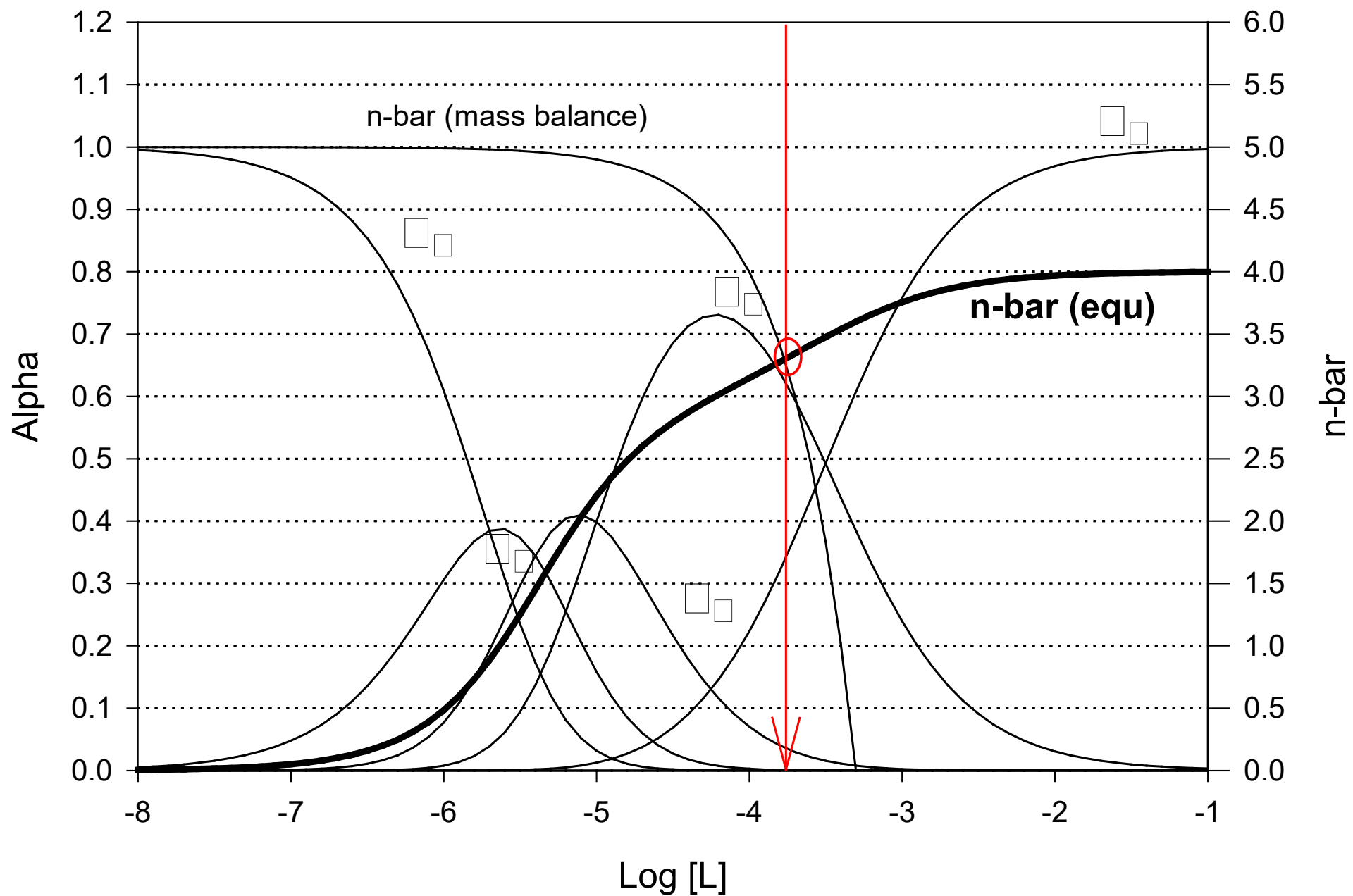
Species	Betas
ZnL	Log $\beta_1 = 5.7$
ZnL ₂	Log $\beta_2 = 11.1$
ZnL ₃	Log $\beta_3 = 16.1$
ZnL ₄	Log $\beta_4 = 19.6$

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

Zn + CN

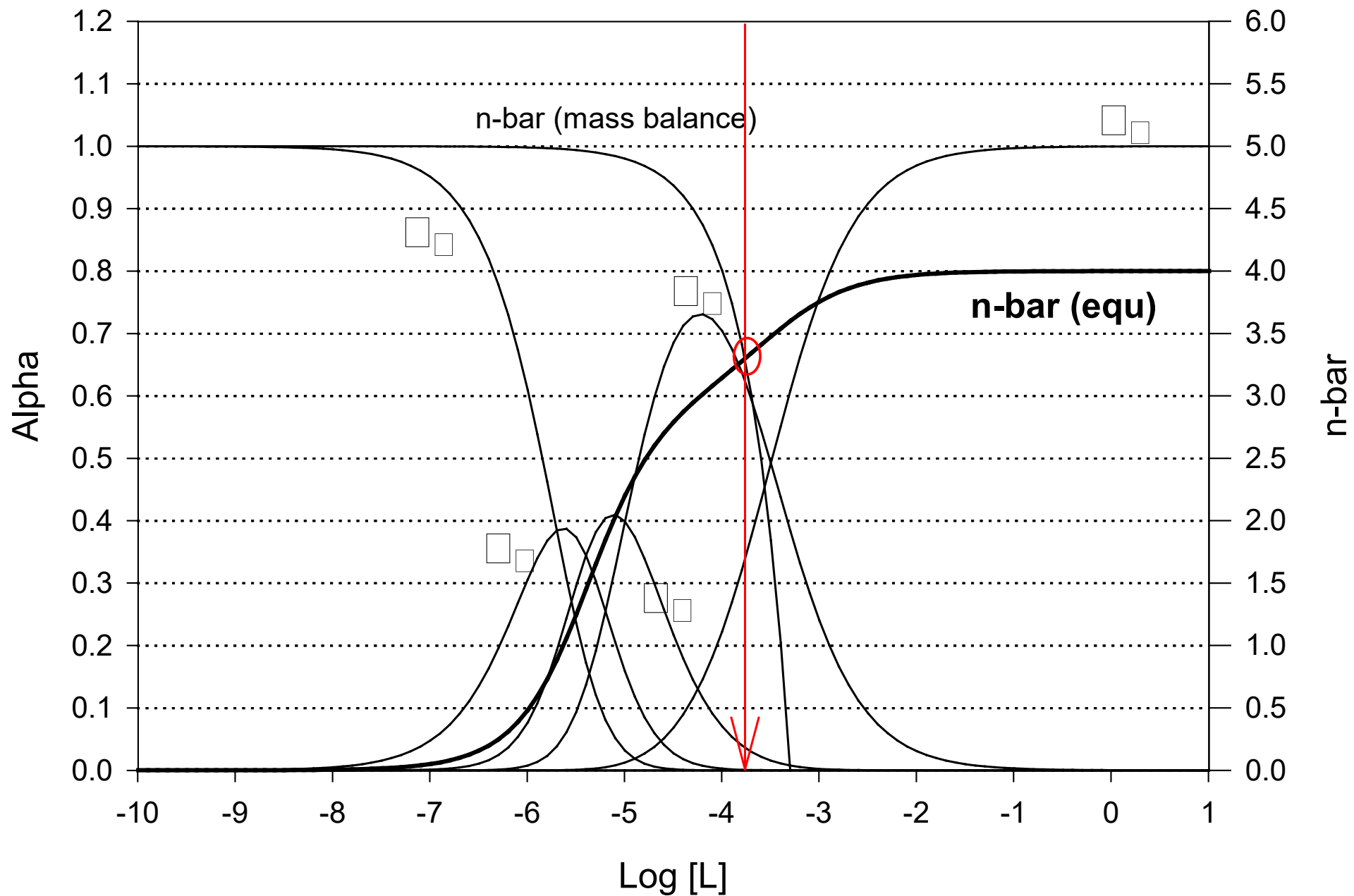


$10^{-4} \text{M Zn}_{\text{Total}} + 5 \times 10^{-4} \text{M CN}_{\text{Total}}$



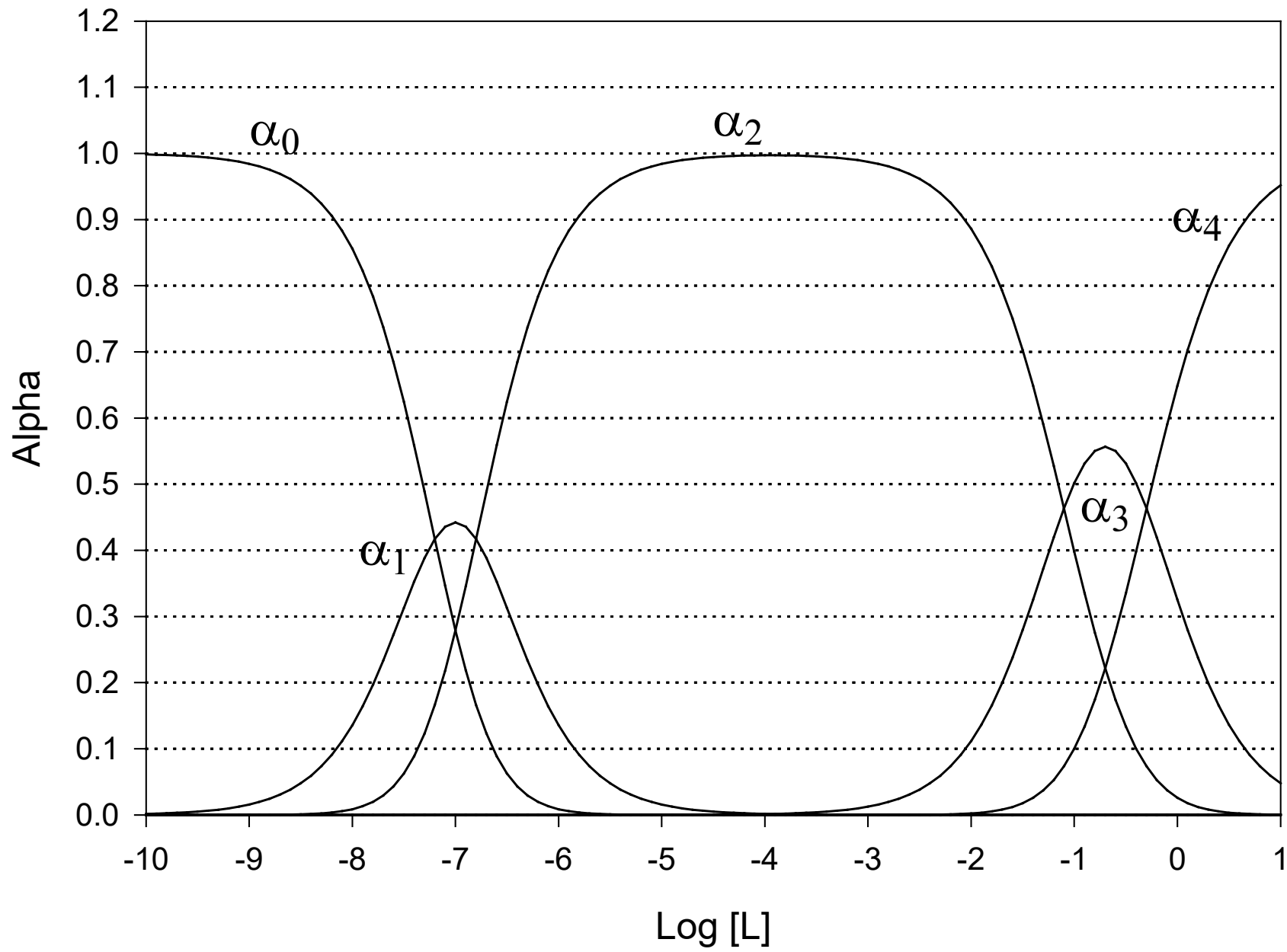
Complexation

$10^{-4}\text{M Zn}_{\text{Total}} + 5 \times 10^{-4}\text{M CN}_{\text{Total}}$



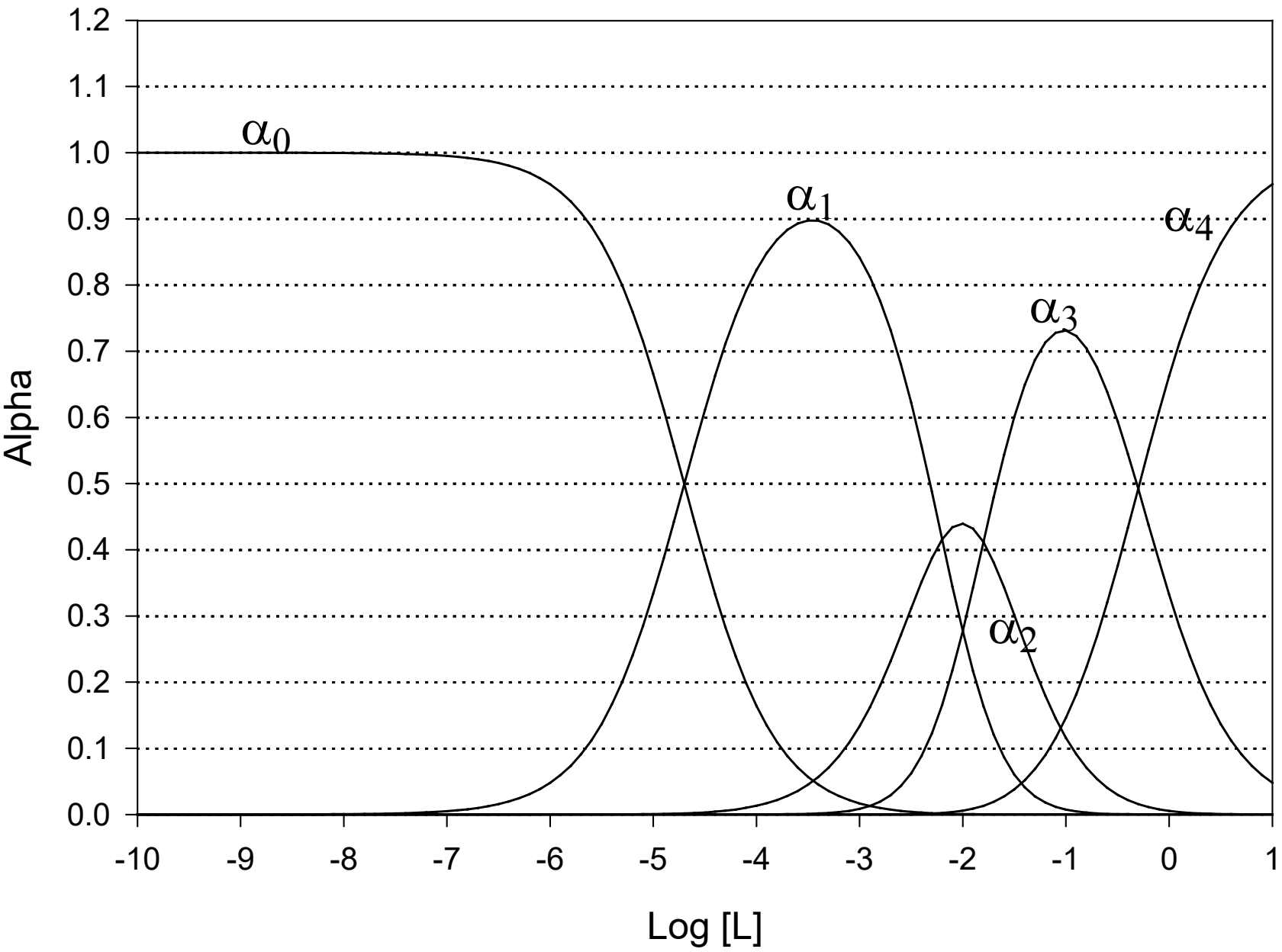
Complexation

$10^{-2}\text{M Hg}_{\text{Total}} + 3 \times 10^{-2}\text{M Cl}_{\text{Total}}$



Complexation

$10^{-2}\text{M Ag}_{\text{Total}} + 10^{-2}\text{M Br}_{\text{Total}}$



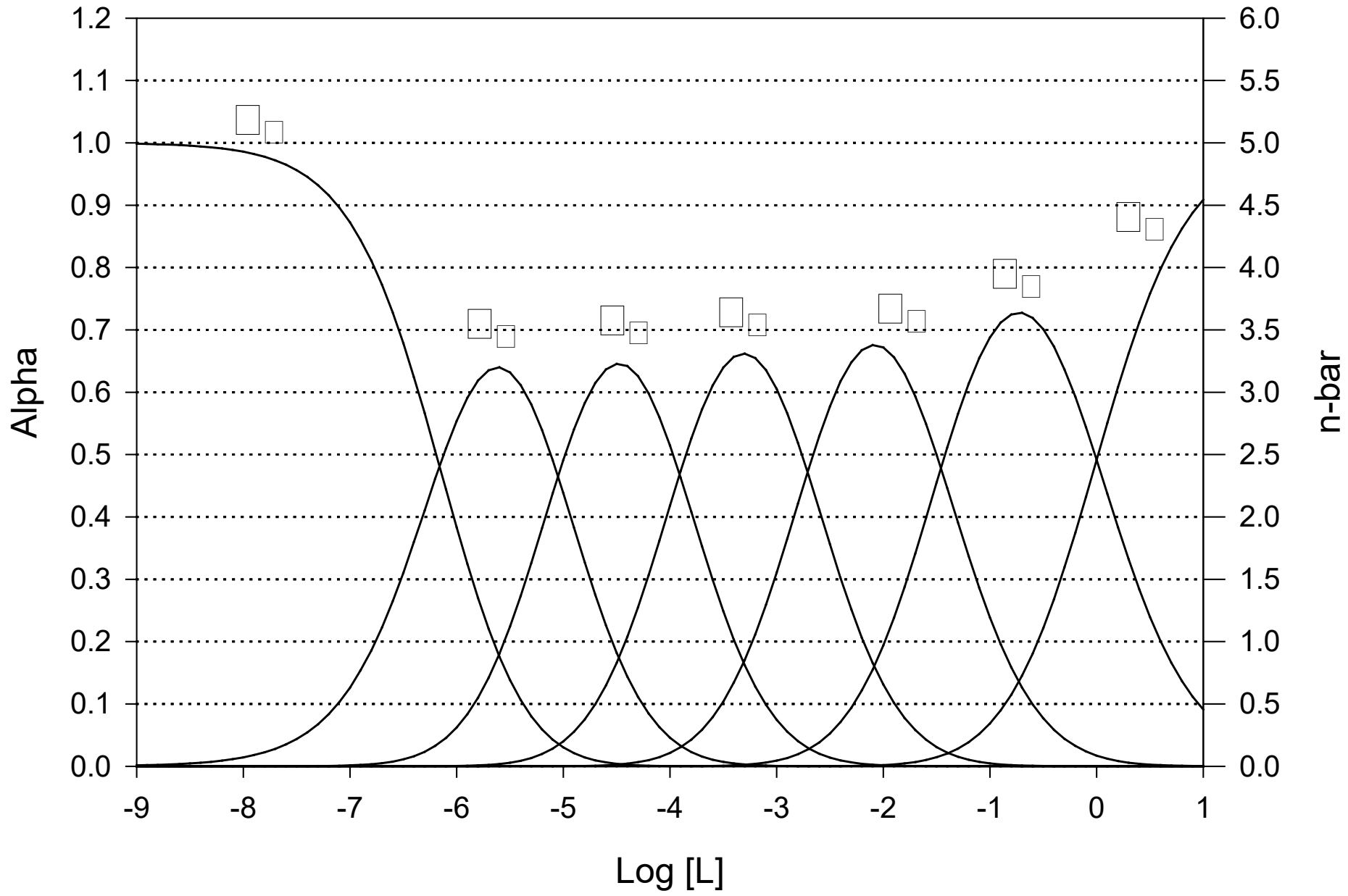
Aluminum Fluoride system

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

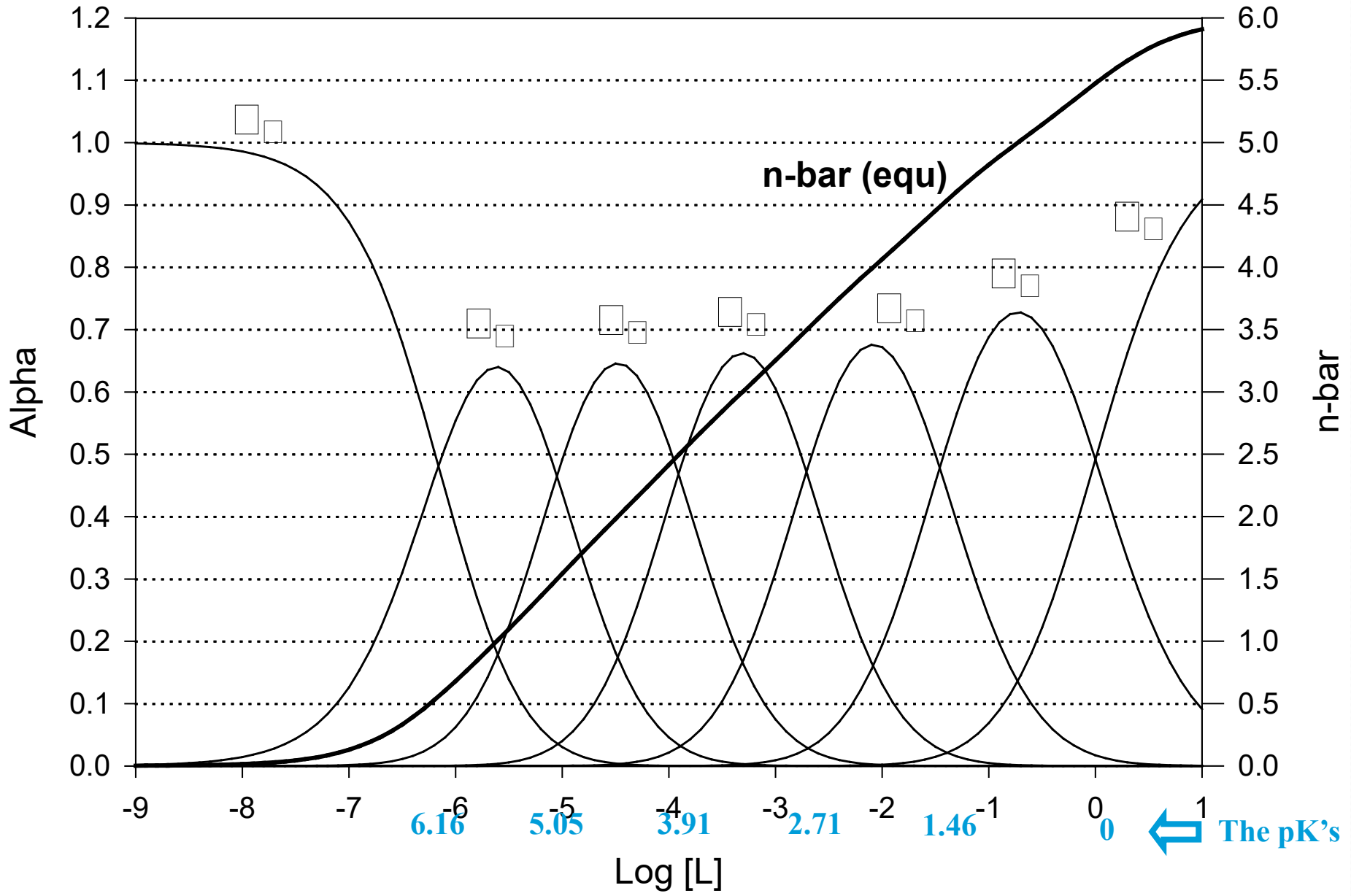
$$\alpha_0 \equiv \frac{[M]}{C_M} = \left(1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n\right)^{-1}$$

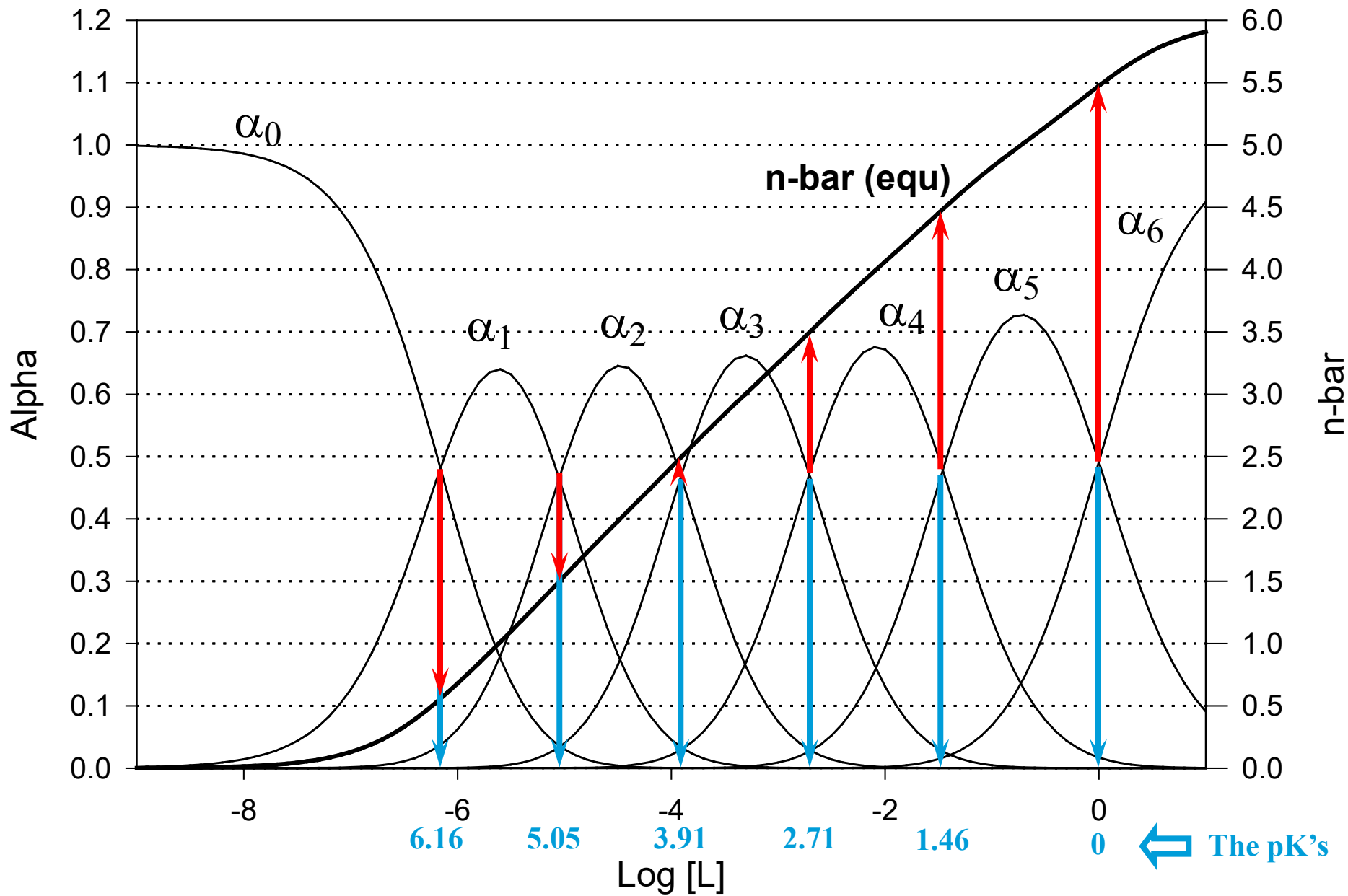
$$\alpha_n \equiv \frac{[ML_n]}{C_M} = \alpha_0 \beta_n [L]^n$$

Aluminum Fluoride



Aluminum Fluoride

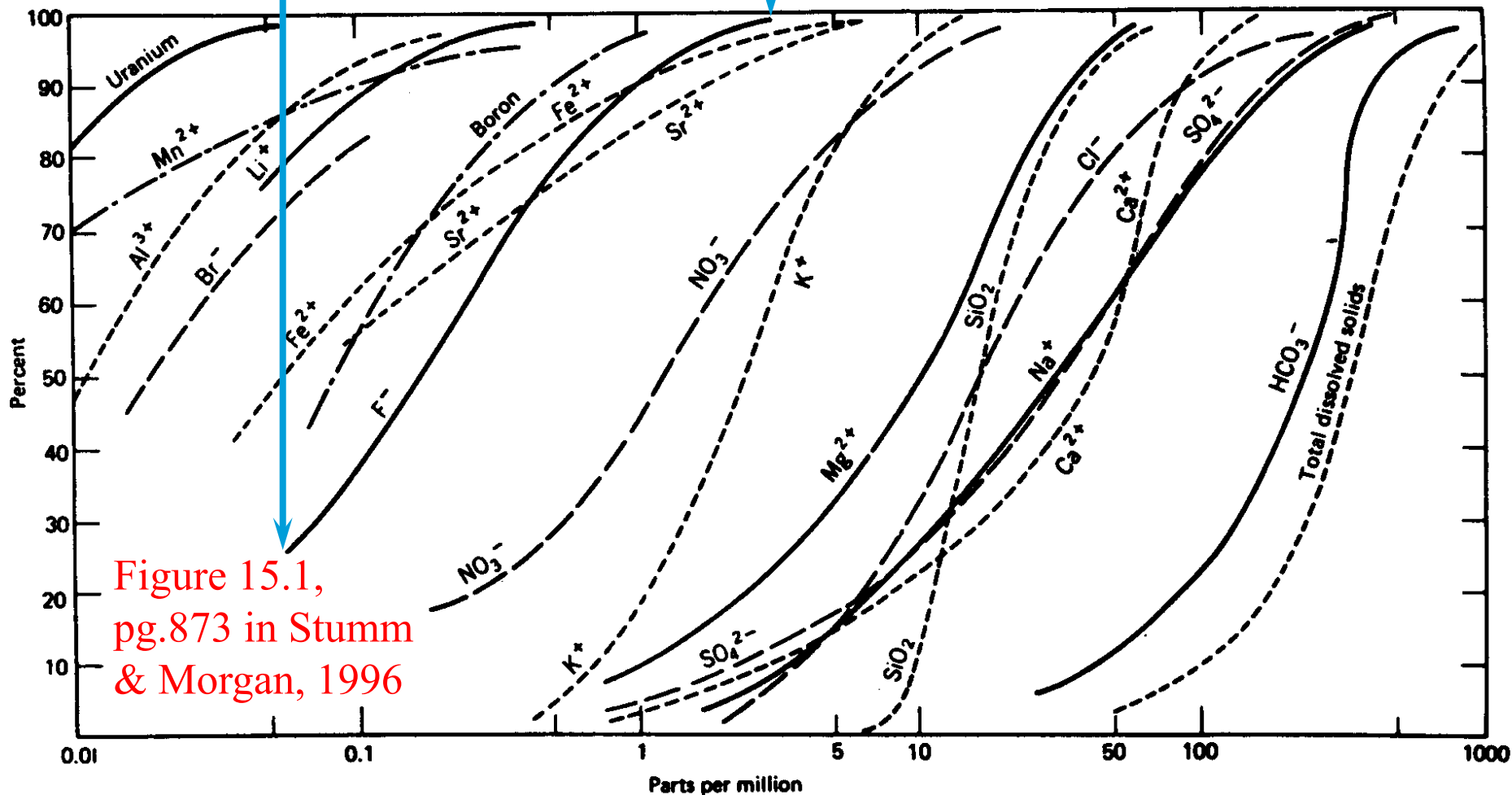




Natural Fluoride

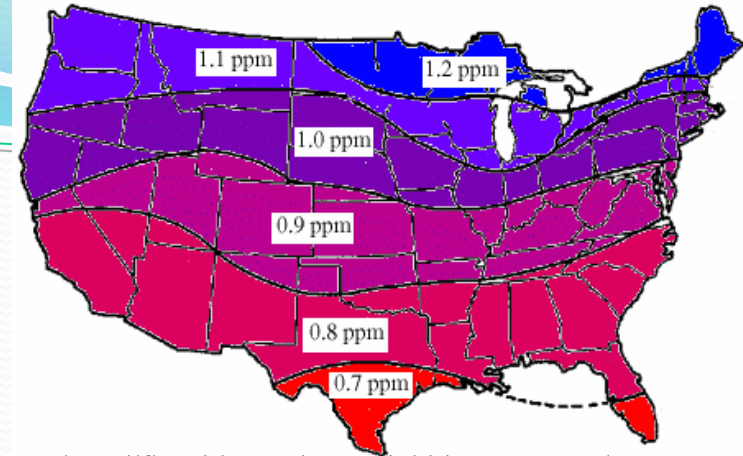
Figure 1.4, pg. 9 in Benjamin, 2015

$10^{-5.5}$ \longleftrightarrow $10^{-3.8}$



Fluoride addition

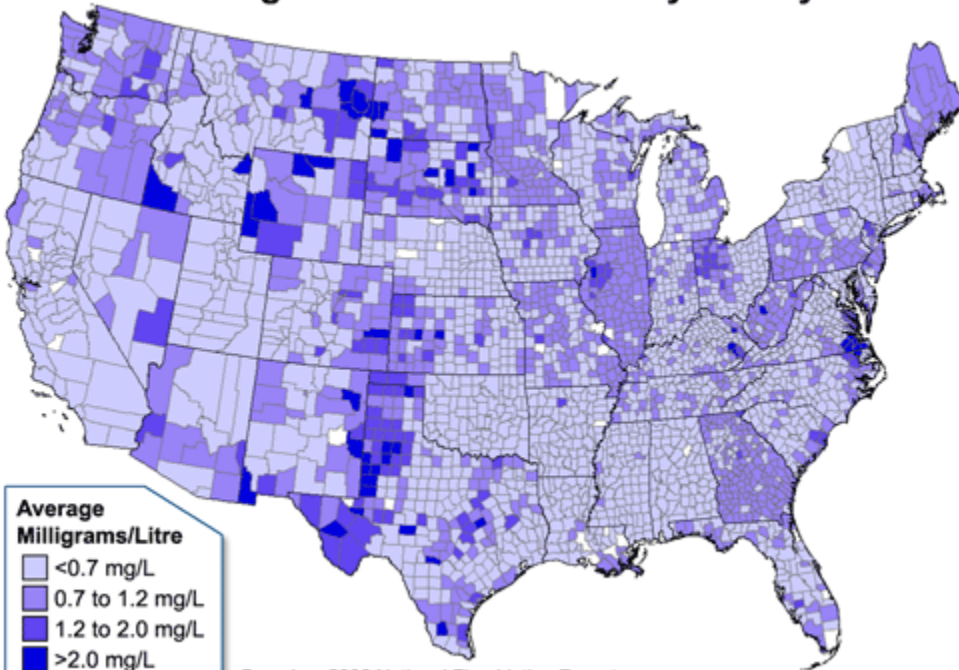
- Balance between Dental Caries and Fluorosis
- Recommended dose
 - 0.7 to 1.2 mg/L, Based on temperature



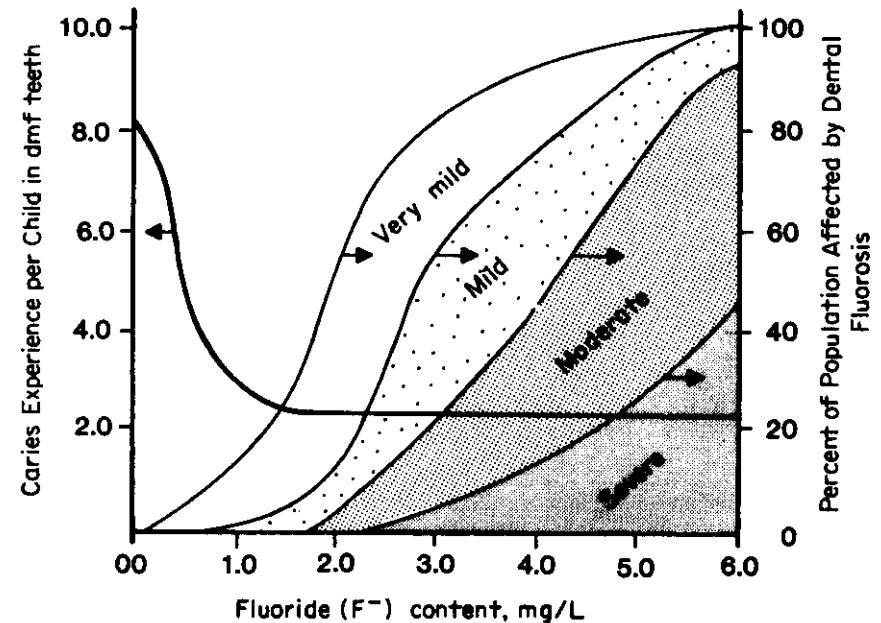
<http://fluoride-math-tutorial.blogspot.com/>

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

Average Fluoridation Levels by County

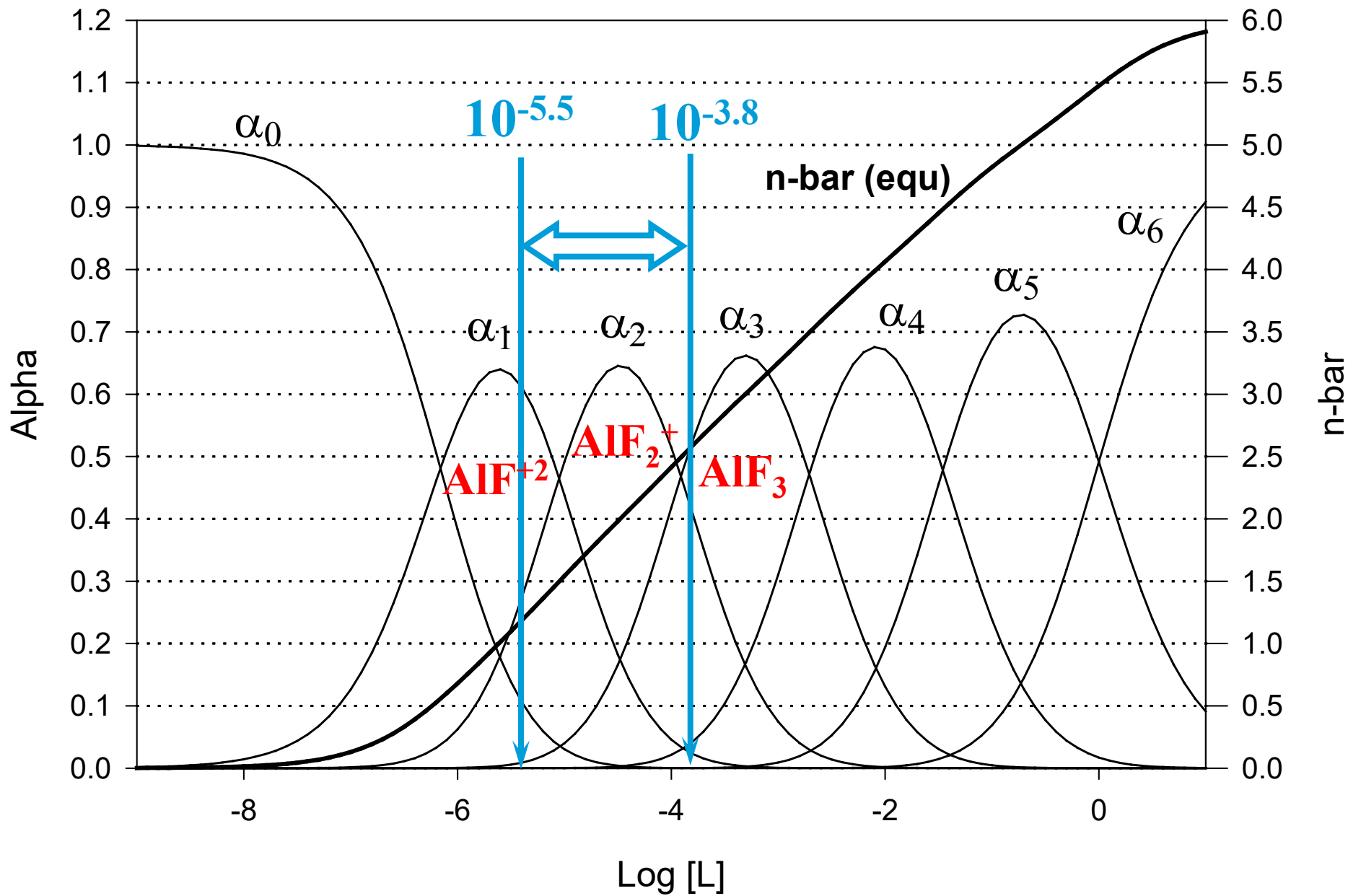


Based on 2006 National Fluoridation Report



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?

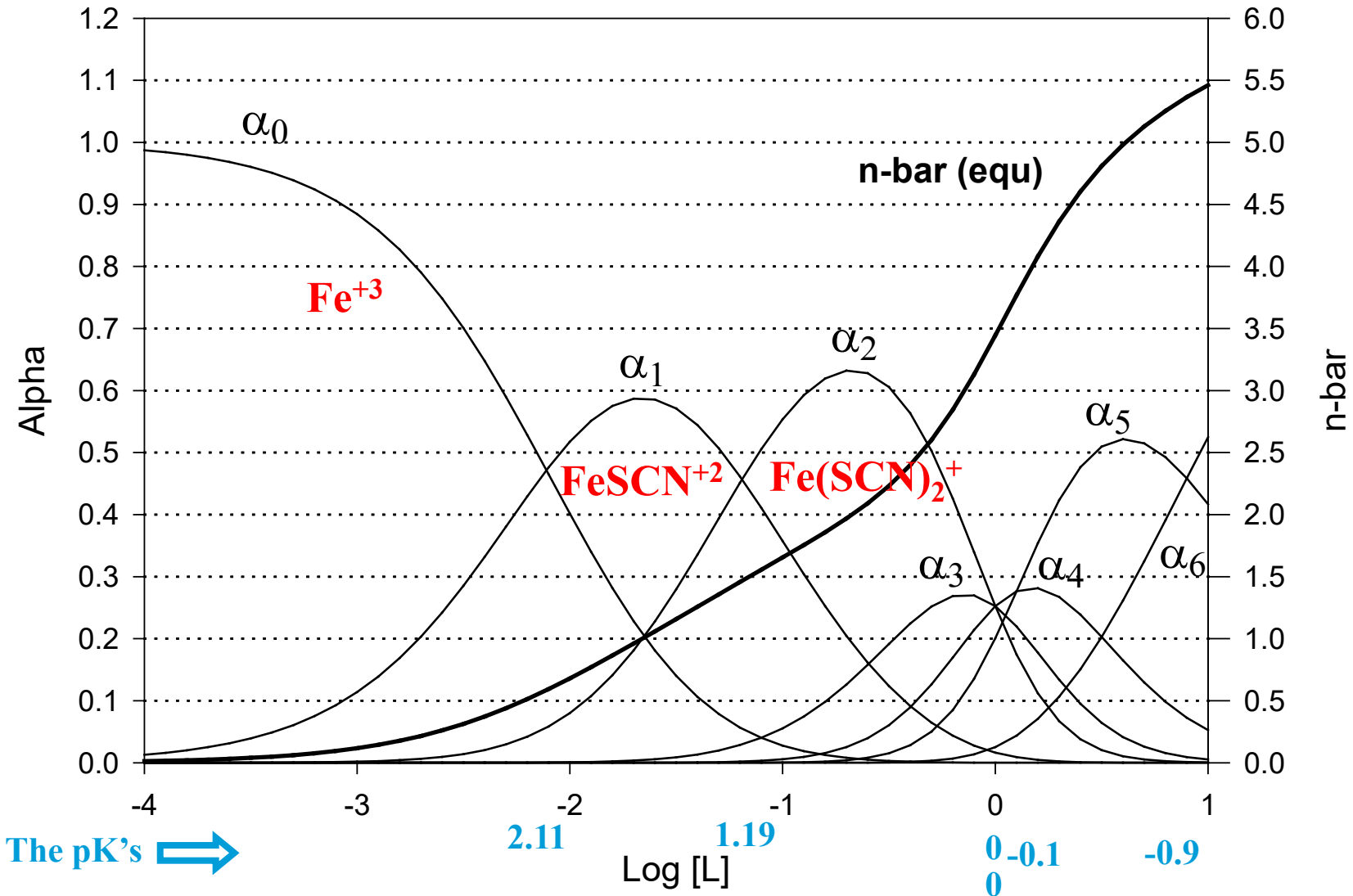


Iron Thiocyanate system

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

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

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



Specific problem

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

Fe-S problem

- Below are the equilibria for the Fe^{+2} – HS system as listed in Benjamin's book. Note that there are no equilibria for FeL , as this species is never significant. Prepare a graph of alpha values (vs $\log[\text{HS}^-]$) for 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 ₂ L		22.25

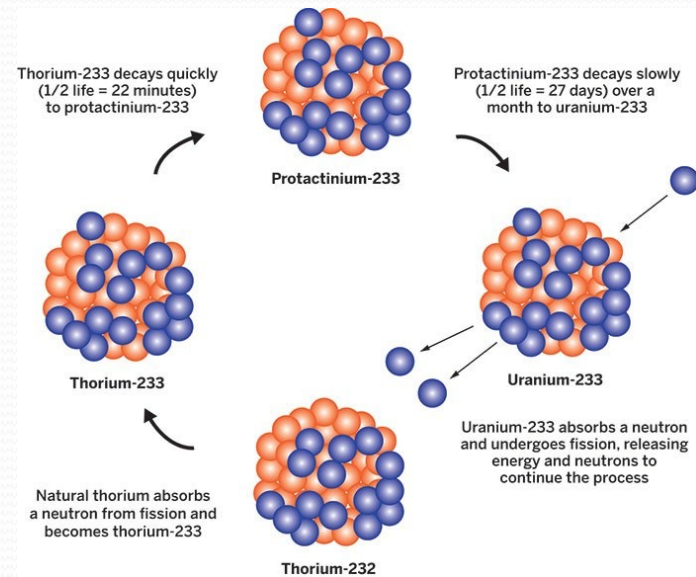
Log β values (From Table 8.3 ; pg 374)

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
 - $^{232}_{90}\text{Th} + n \rightarrow ^{233}_{90}\text{Th} + \gamma \rightarrow ^{233}_{91}\text{Pa} \rightarrow ^{233}_{92}\text{U}$
- 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.

$$1 \text{ Ci} = 3.7 \times 10^{10} \text{ dps}$$



Converting pCi/L to ug/L

- Spreadsheet calculation for Thorium-232

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

Thorium: Actinide Element

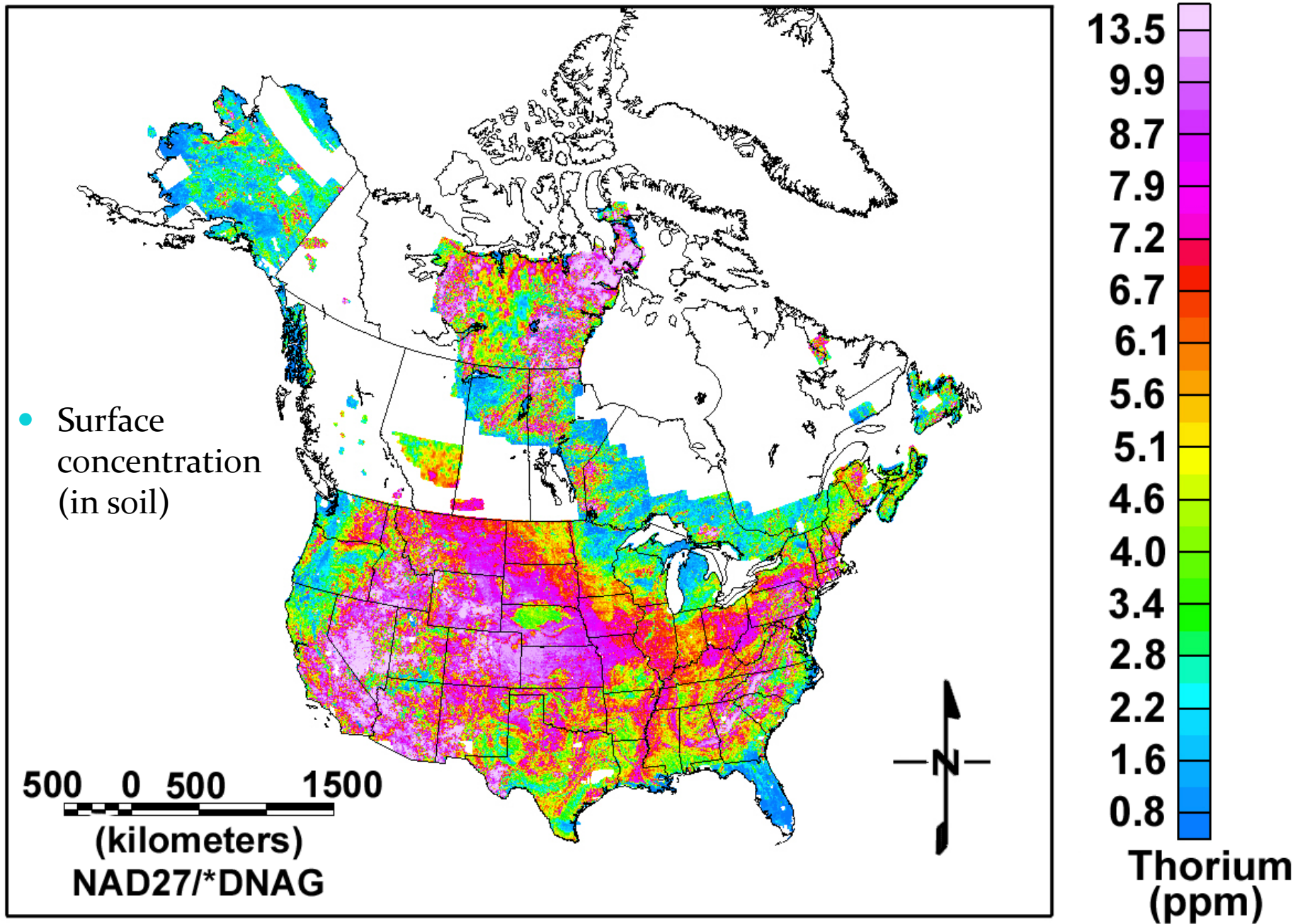
Periodic Table of the Elements

1 IA 11A																	18 VIIIA 8A
1 H Hydrogen 1.008	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.09	35 Br Bromine 79.904	36 Kr Krypton 84.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinide Series	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [293]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide
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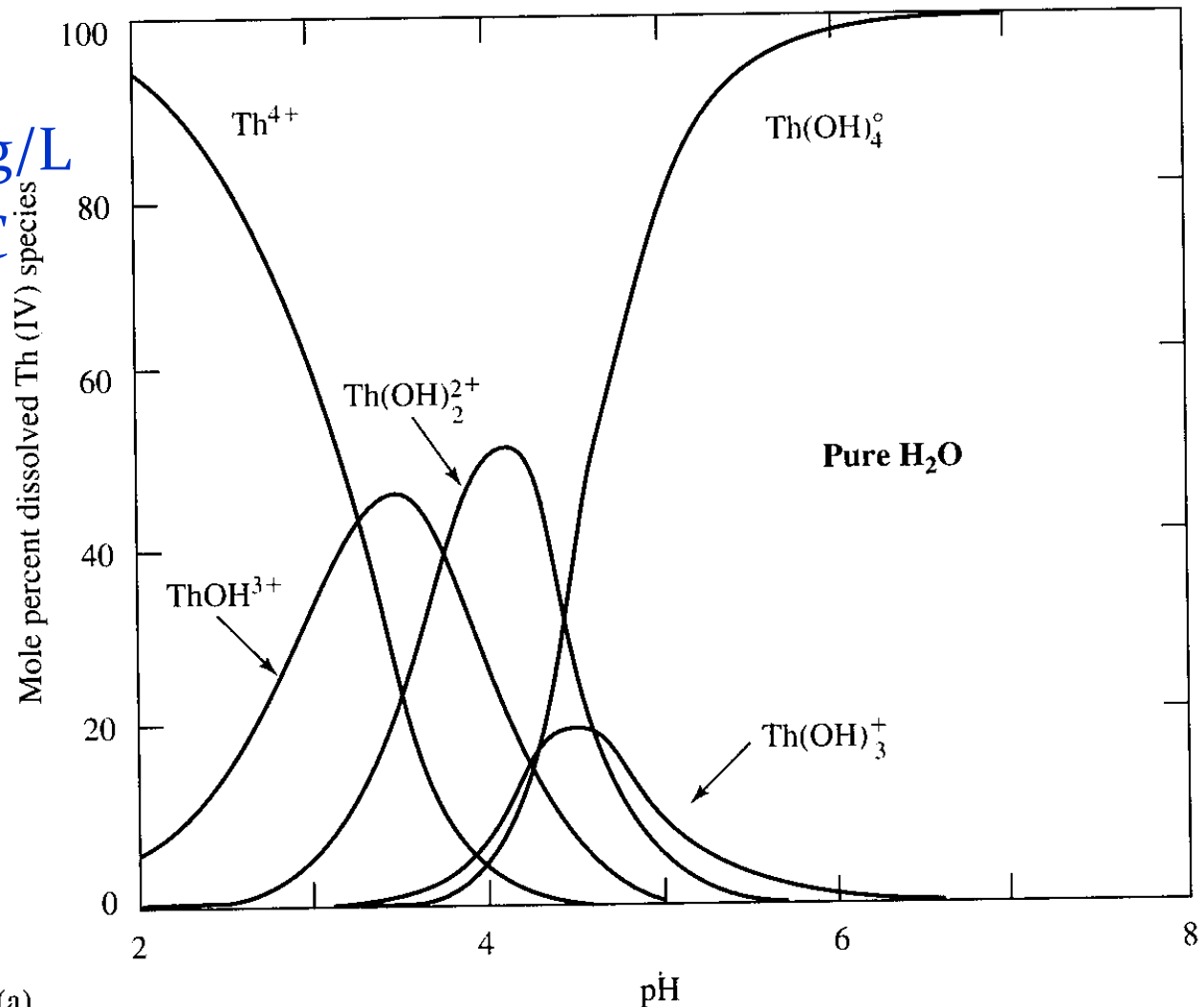
Thorium Concentrations



Thorium example I

- In pure water
 - $C_{\text{Th}} = 0.01 \mu\text{g/L}$
 - $\text{Temp} = 25^\circ\text{C}$

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



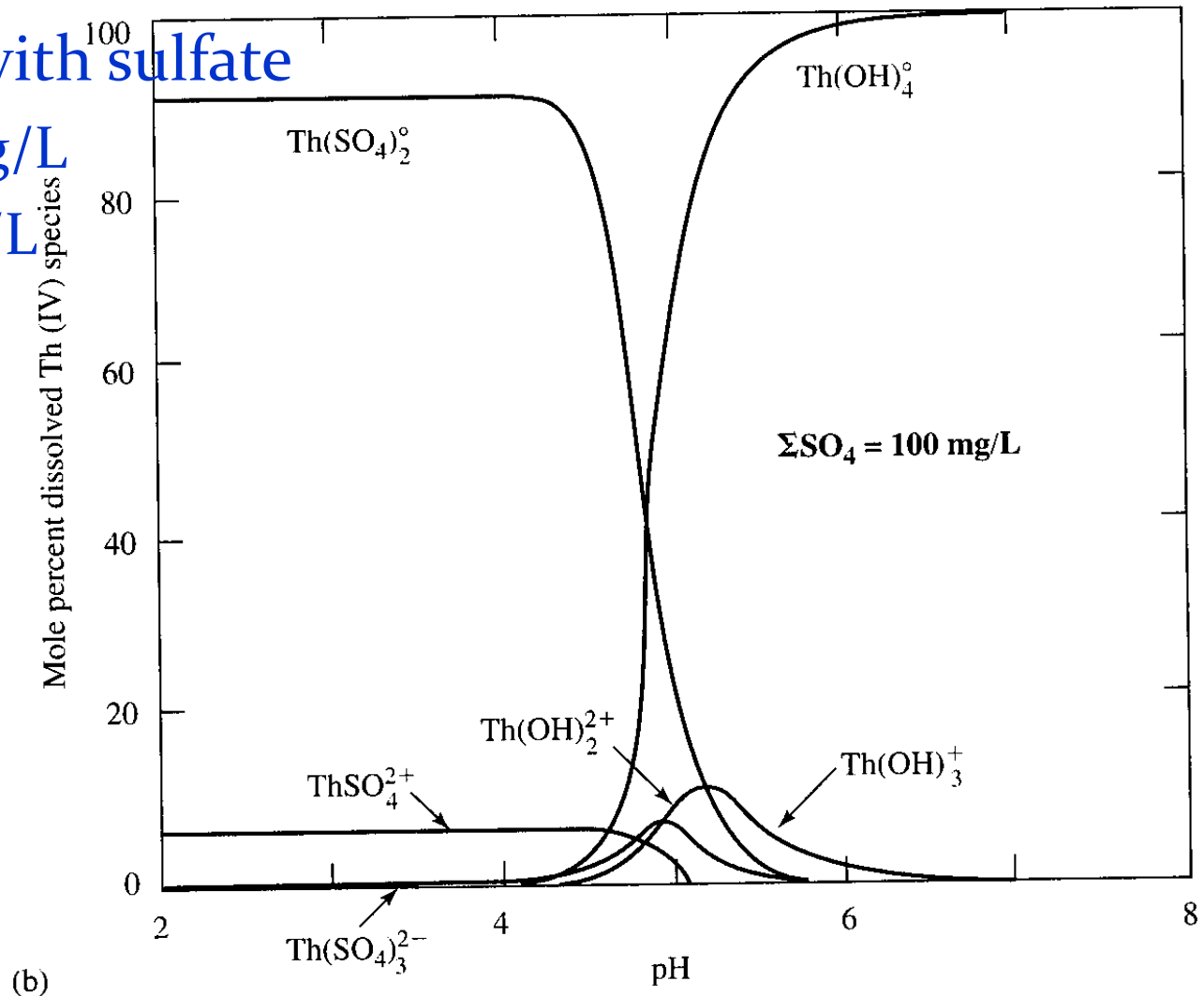
Thorium example II

- In pure water with sulfate

- $C_{\text{SO}_4} = 100 \text{ mg/L}$
- $C_{\text{Th}} = 0.01 \text{ } \mu\text{g/L}$
- $\text{Temp} = 25^\circ\text{C}$

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

David Reckhow



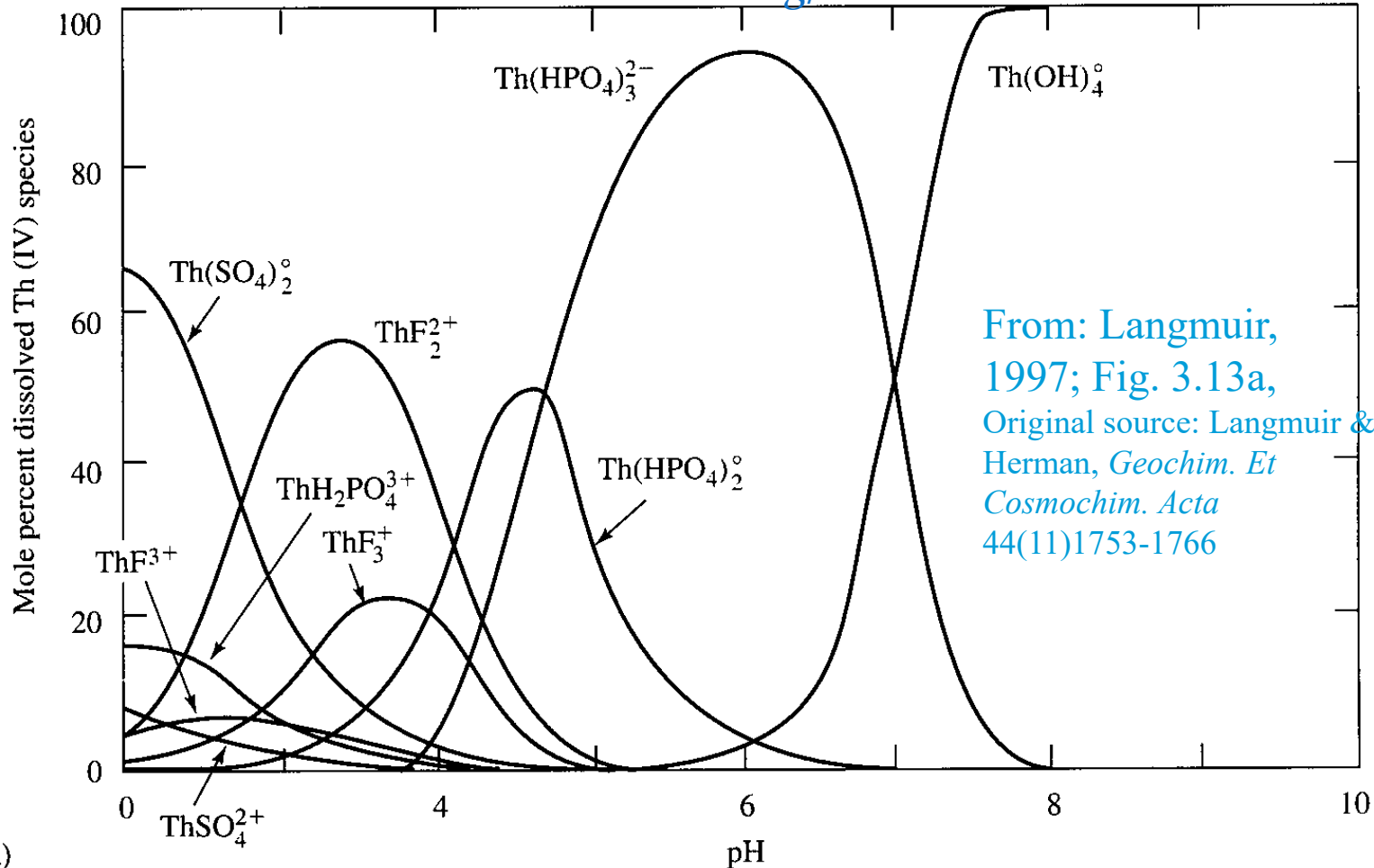
Model groundwater without organics

- $C_{\text{Th}} = 0.01 \mu\text{g/L}$ & Temp = 25°C
- 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

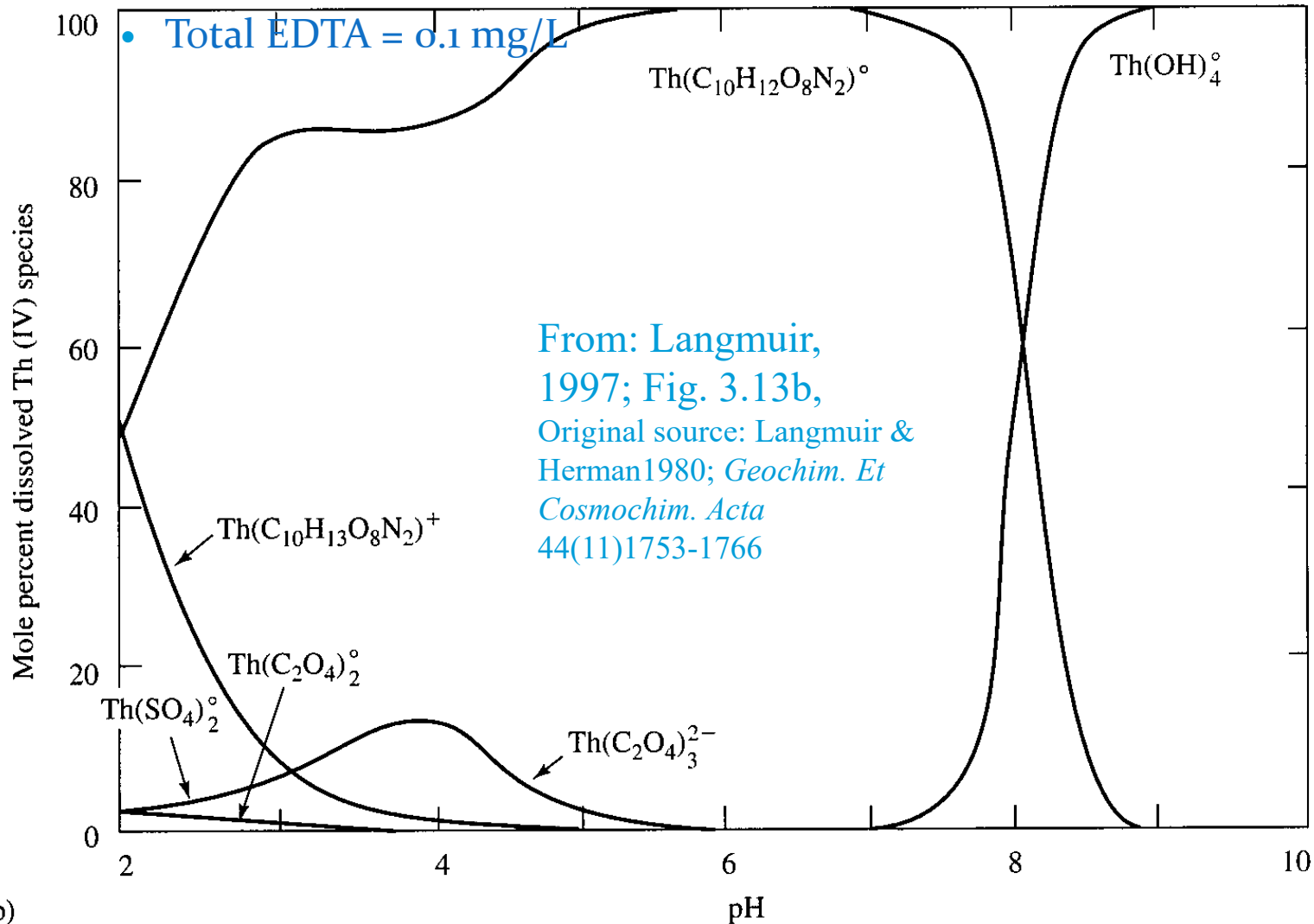
Th-P solids
are less
bioavailable

Thorium example III

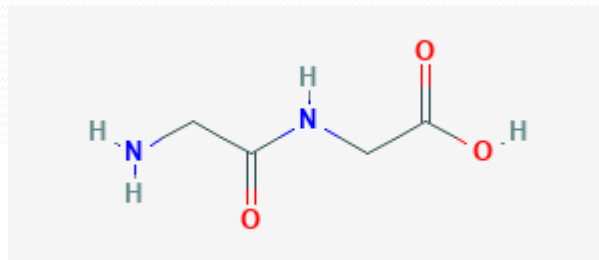


- Model groundwater with organics
 - Same inorganic groundwater composition
 - With organics
 - Total oxalate = 1.0 mg/L
 - Total EDTA = 0.1 mg/L

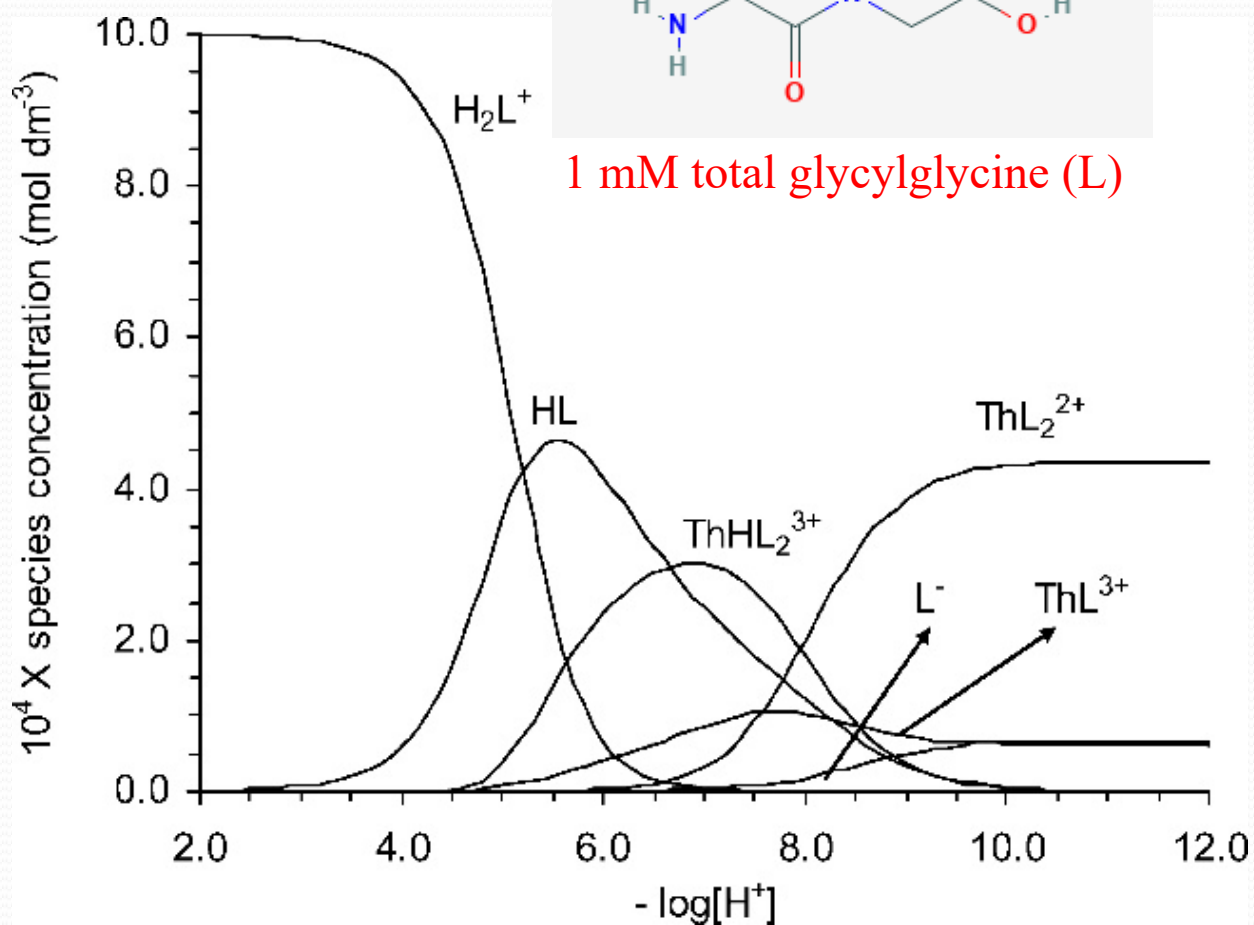
Thorium example IV



In the human body



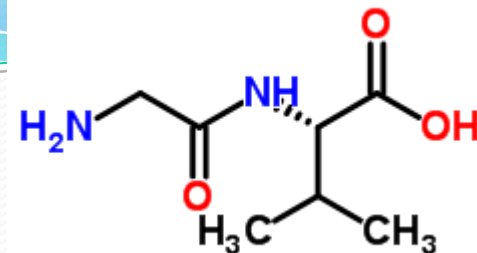
1 mM total glycylglycine (L)



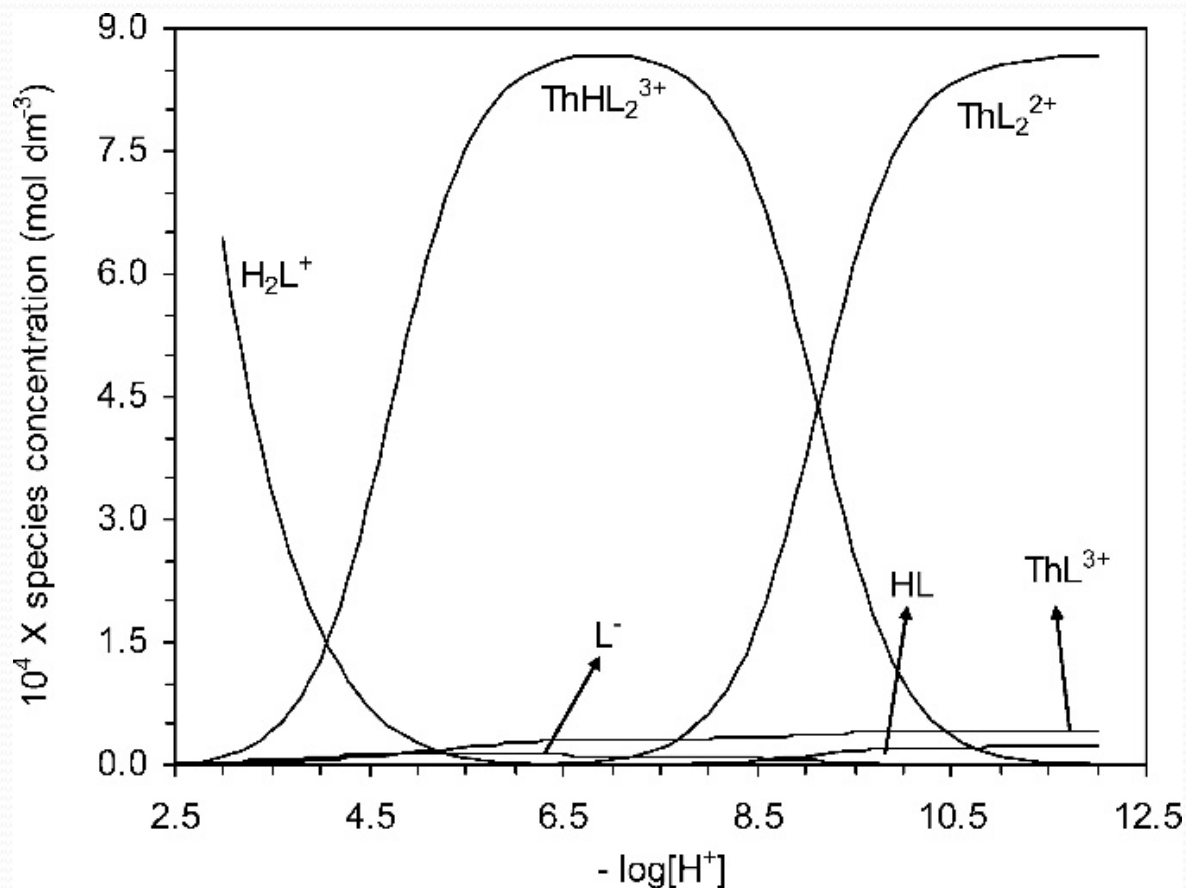
- “The thorium(IV) ion readily reacts with in vivo amino acids, peptides, nucleic acids, proteins, etc. to form stable complexes which are distributed in the body, primarily in the liver, bone, and kidneys”

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 there are no equilibria for FeL , as this species is never significant. Prepare a graph of alpha values (vs $\log[\text{HS}^-]$) for 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 ₂ L		22.25

Log β values (From Table 8.3 ; pg 374)

Calculations

Log β values (From Table 8.3 ; pg 374)

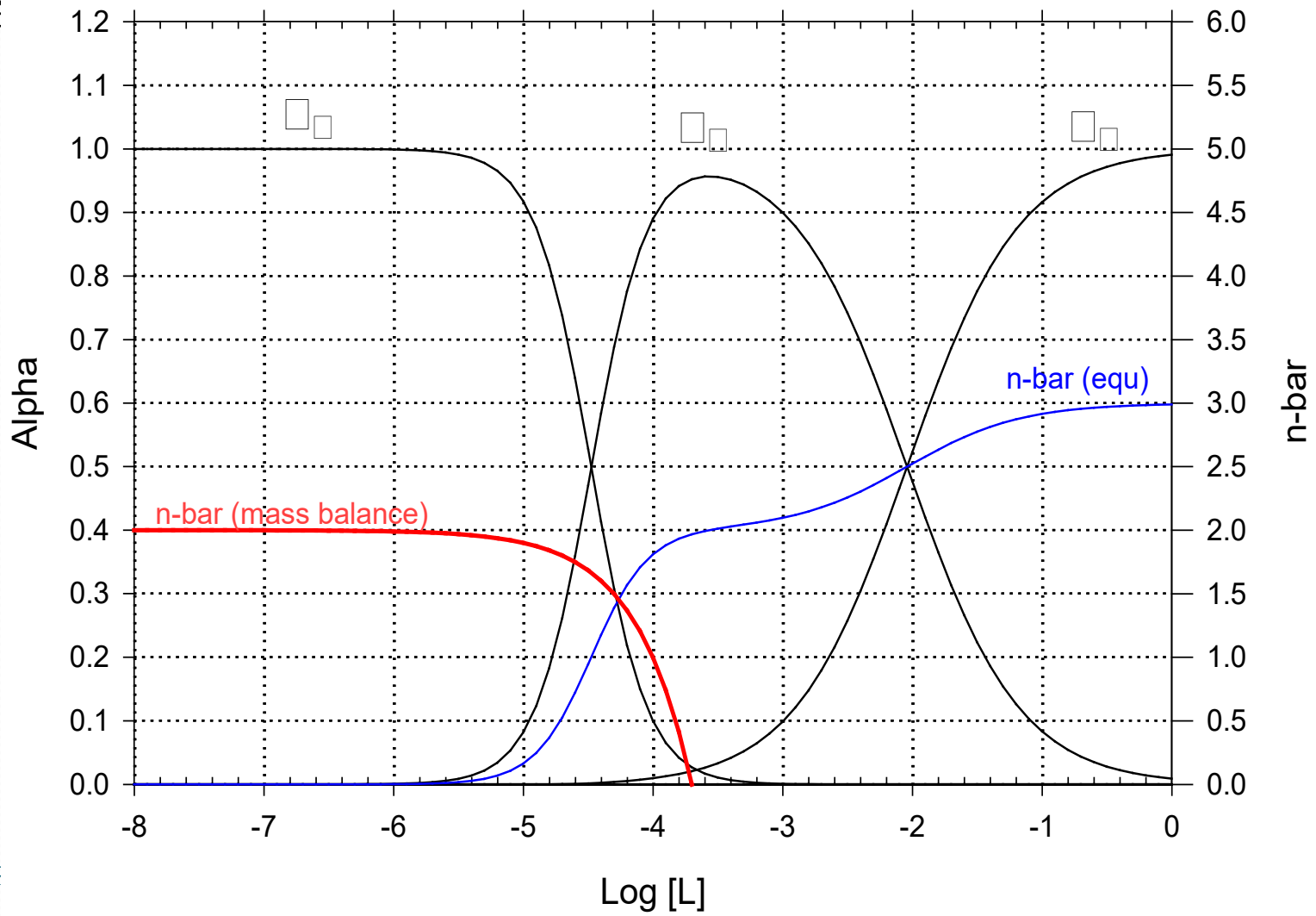
- calculations

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

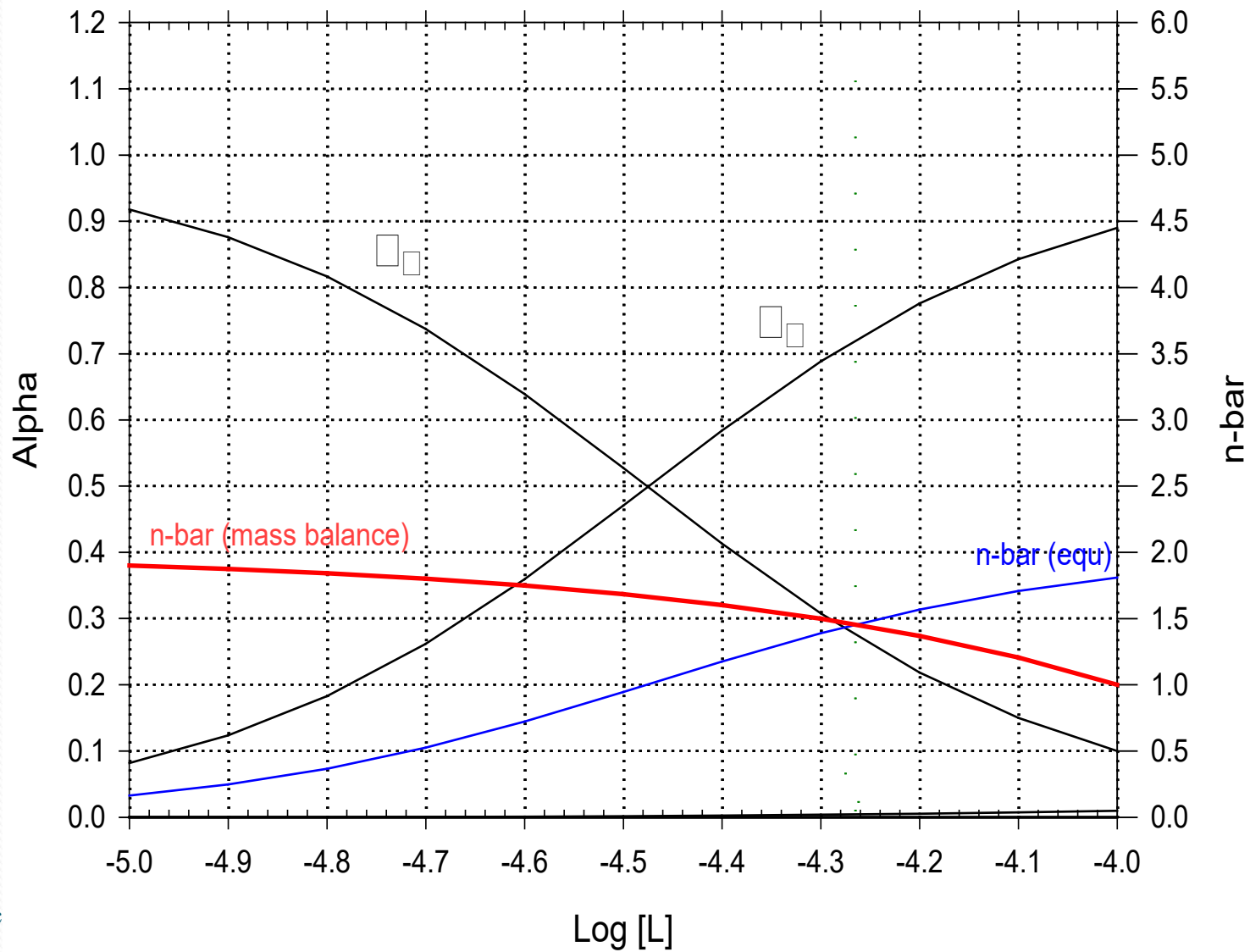
$$\beta_3 = 10^{10.99} = \frac{[FeL_3]}{[Fe] [L^3]}$$

Species	Ligand	
	HS-	PO ₄ ⁻³
FeL ₂	8.95	
FeL ₃	10.99	
FeH ₂ L		22.25

● α



● a



Species	Conc (M)	Log C
HS ⁻	5.37E-05	-4.27
Fe ⁺²	2.70E-05	-4.57
Fe(HS) ₂ ⁰	7.30E-05	-4.14
Fe(HS) ₃ ⁻	0	
H ⁺	1.00E-08	-8
OH ⁻	1.00E-06	-6
H ₂ S	5.75E-06	-5.24
S ⁻²	5.37E-11	-10.27