Updated: 11 March 2020

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CEE 680: Water Chemistry

Lecture #29

Complexation: Speciation in Fresh Waters

(Stumm & Morgan, Chapt.6: pg.289-305)

Benjamin; Chapter 8.1-8.6

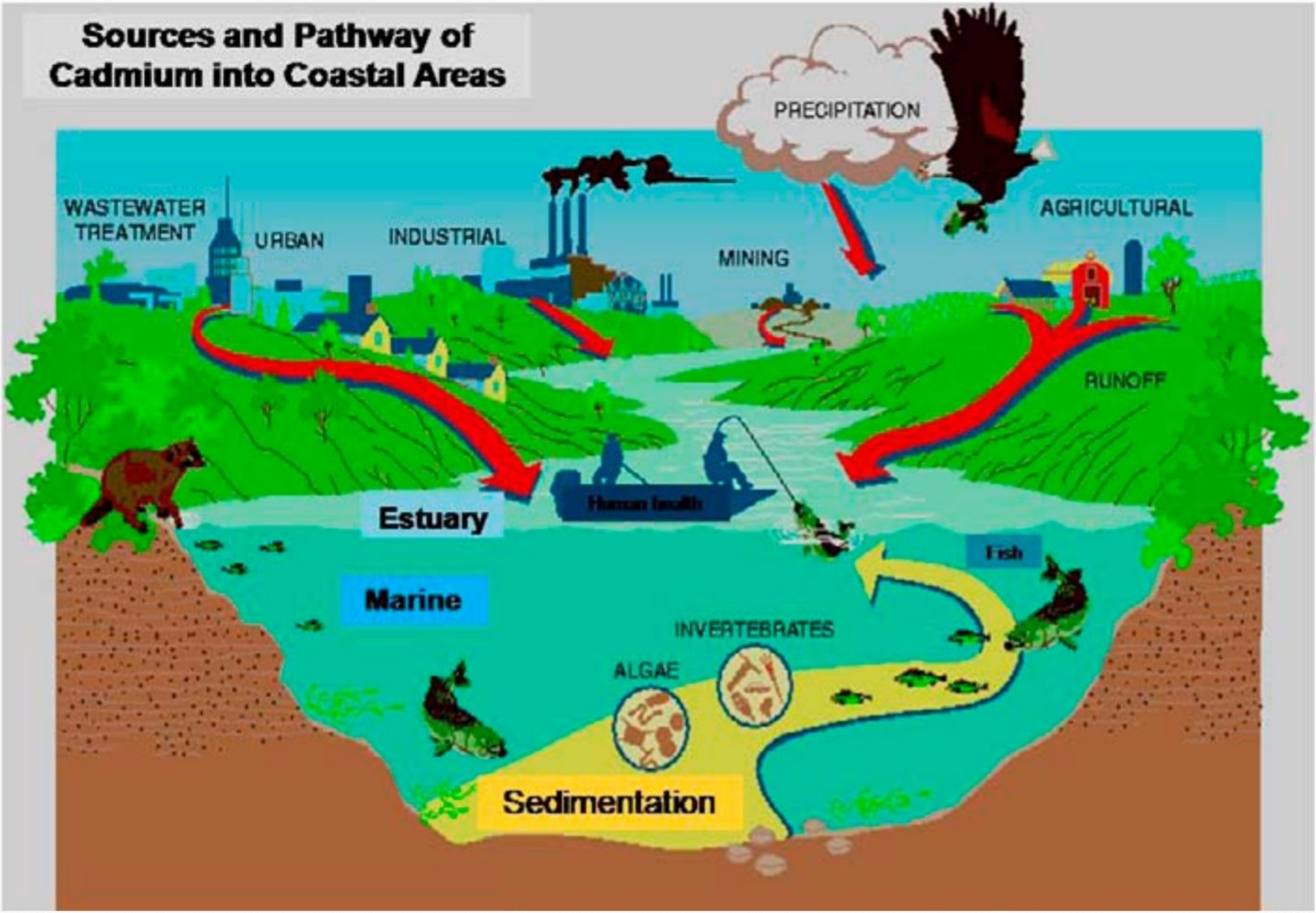
Cadmium

- Batteries & electroplating
- Very high ratio of abundance to toxicity
  - Like Pb, Hg, As
- EPA Standards
  - 0.005 µg/L in drinking water
    - Concern over kidney damage

Click here for more on Cd

Cadmium is of no use to the human body and is toxic even at low levels. The negative effects of cadmium on the body are numerous and can impact nearly all systems in the body, including cardiovascular, reproductive, the kidneys, eyes, and even the brain.

- Cadmium affects blood pressure.
- Cadmium affects prostate function and testosterone levels.
- Cadmium induces bone damage (Itai-ltai).
- Exposure to cadmium can affect renal and dopaminergic systems in children.



Sources and Pathway of Cadmium into Coastal Areas
PRECIPITATION
WASTEWATER TREATMENT
URBAN
INDUSTRIAL
MINING
AGRICULTURAL
RUNOFF
Estuary
Fish
Marine
INVERTEBRATES
ALGAE
Sedimentation

- Flux in 10^7 M/yr

From: Morel & Malcolm, "*The Biogeochemistry of Cadmium*", Chapt 8 in Metal Ions in Biological Systems, Vol 43 Sigel, Sigel & Sigel, eds.

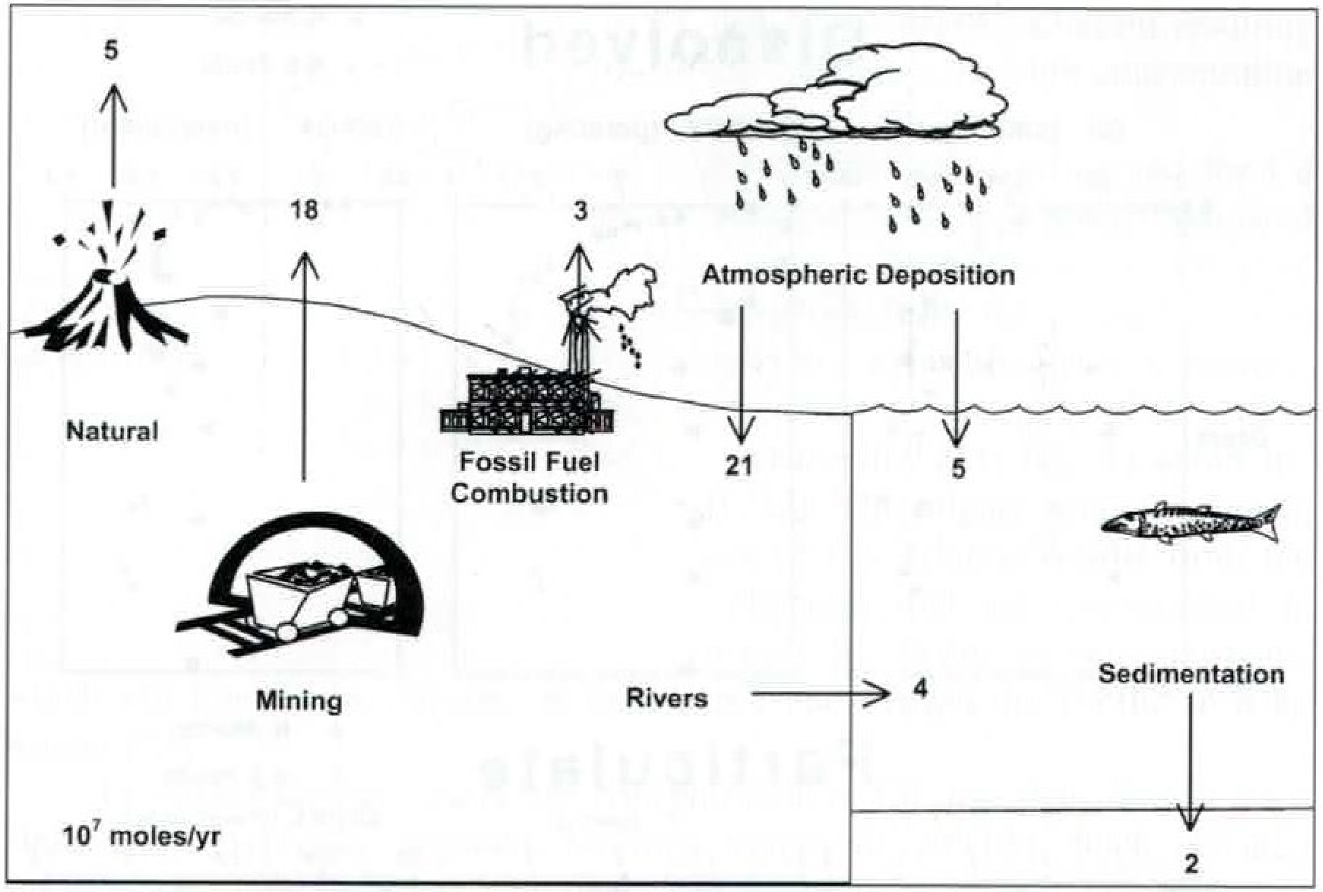


Figure 3 Flux estimates of the global cadmium cycle. All fluxes are $\times 10^7$ mol year^{-1}. Emissions to the atmosphere are from Ref. [2], mining/smelting flux also from Ref. [16]. Atmospheric deposition and net river input (gross—loss to estuaries) to the ocean are from Ref. [18]. Loss of oceanic cadmium to marine sediments is scaled up from a cadmium accumulation rate of 0.006 nmol cm^{-2} year^{-1} for the Pacific from Ref. [18] and is highly uncertain. (A mass balance is not expected since the atmospheric and riverine inputs include anthropogenic increases that are recent compared to the residence time of Cd in the oceans.) Atmospheric deposition to land was calculated based on the steady-state assumption that emissions to the atmosphere equal losses to the ocean and land.

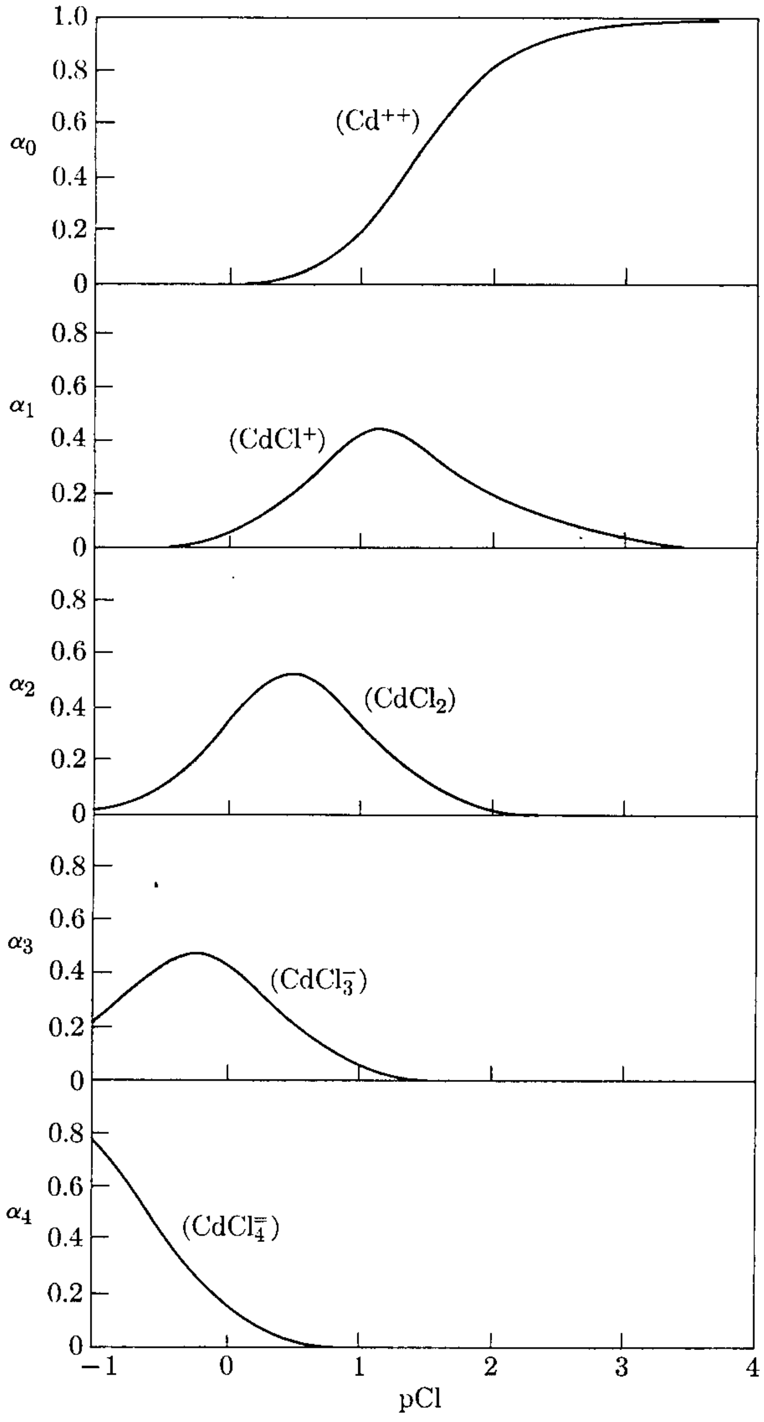
CdCl Example

- Consider the speciation of cadmium and chloride
  - First the four beta's

Reaction	β-value
$Cd^{+2} + Cl^{-} = CdCl^{+}$	21
$Cd^{+2} + 2Cl^{-} = CdCl_2$	166
$Cd^{+2} + 3Cl^{-} = CdCl_3^{-}$	204
$Cd^{+2} + 4Cl^{-} = CdCl_4^{-2}$	71.5

  - Now plot the alpha curves

Cadmium Chloride



From: Butler, 1964; pg.268

Reproduced in Langmuir, 1997; pg.96

Similar to: Butler, 1998; pg.241

CdCl Example

- Calculate the concentration of all species for the following solution
  - 0.01 M $Cd(NO_3)_2$ + 1 M HCl
- Use the equilibrium equations

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

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

  - But what do you use for [L]?

Cadmium Chloride

From: Butler, 1964; pg.268

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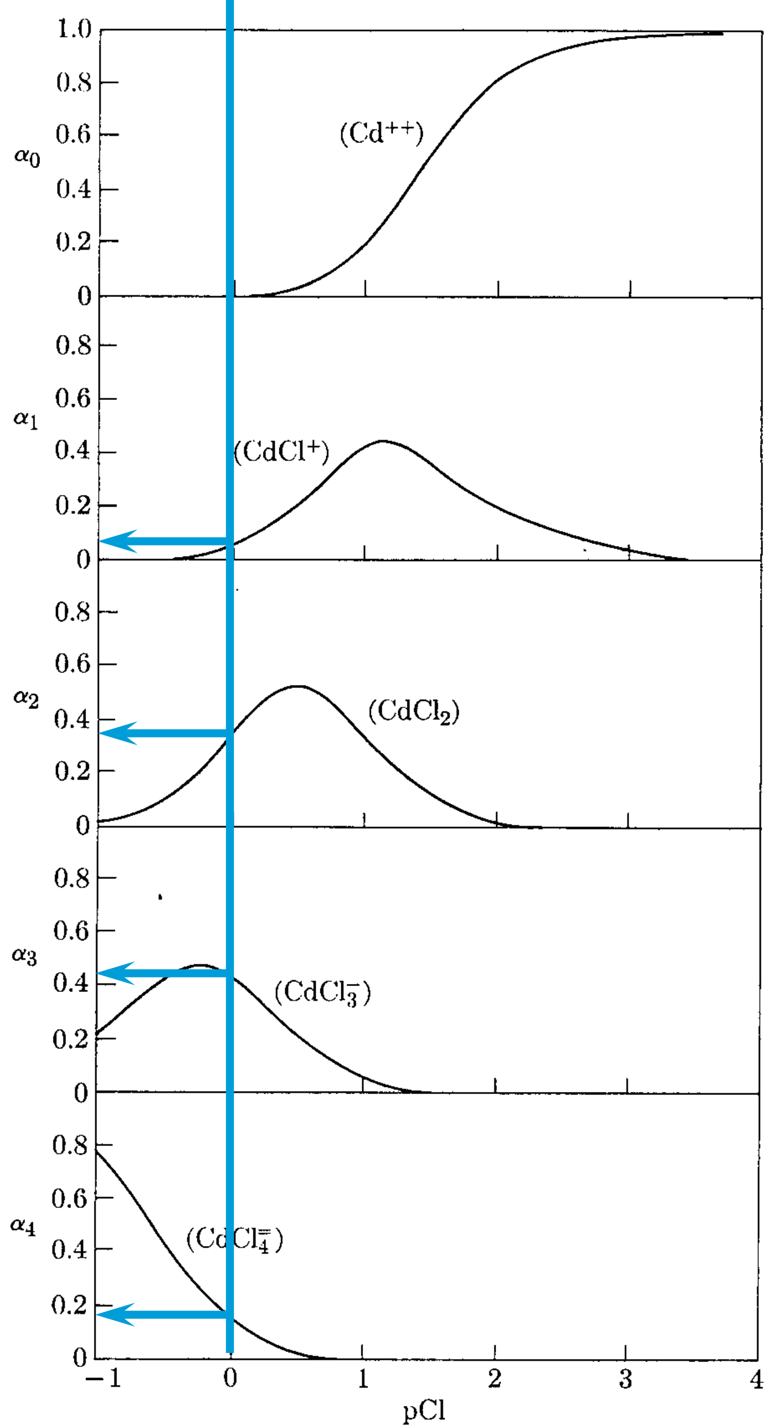
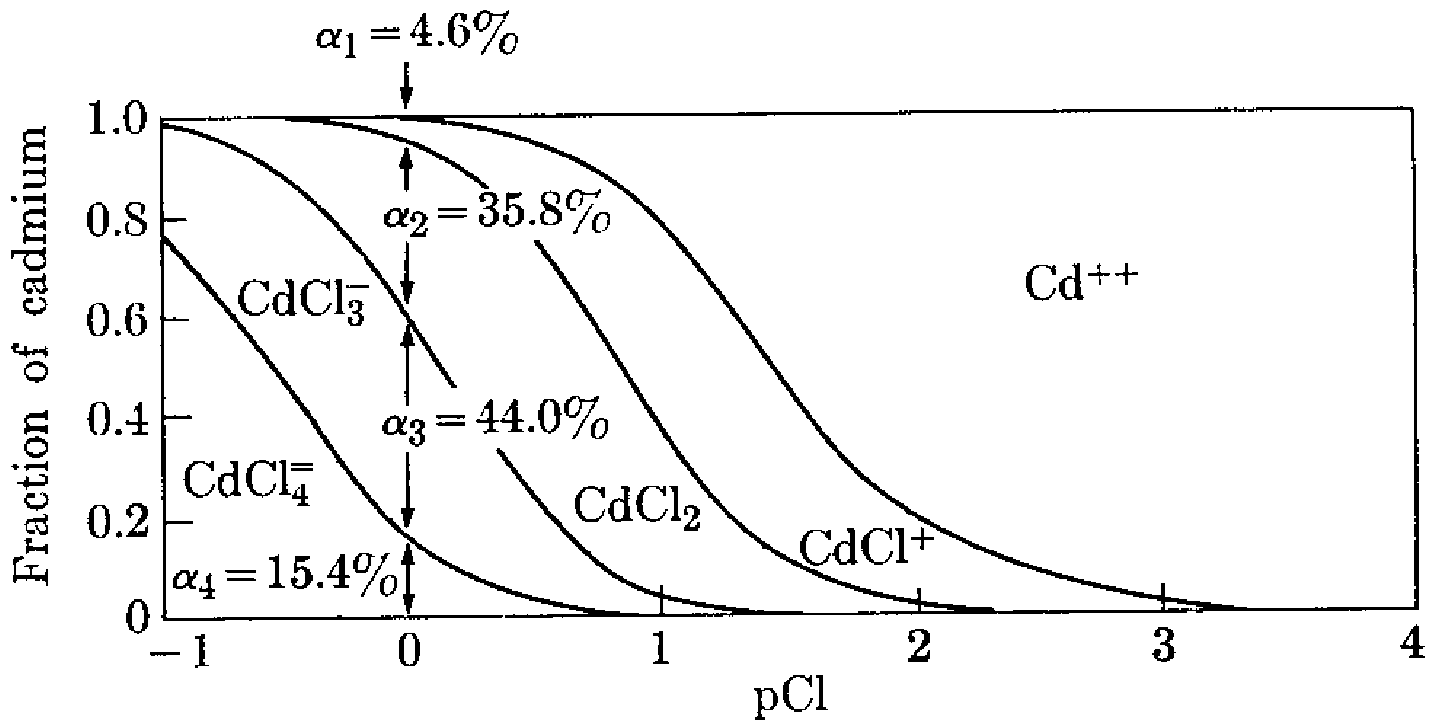
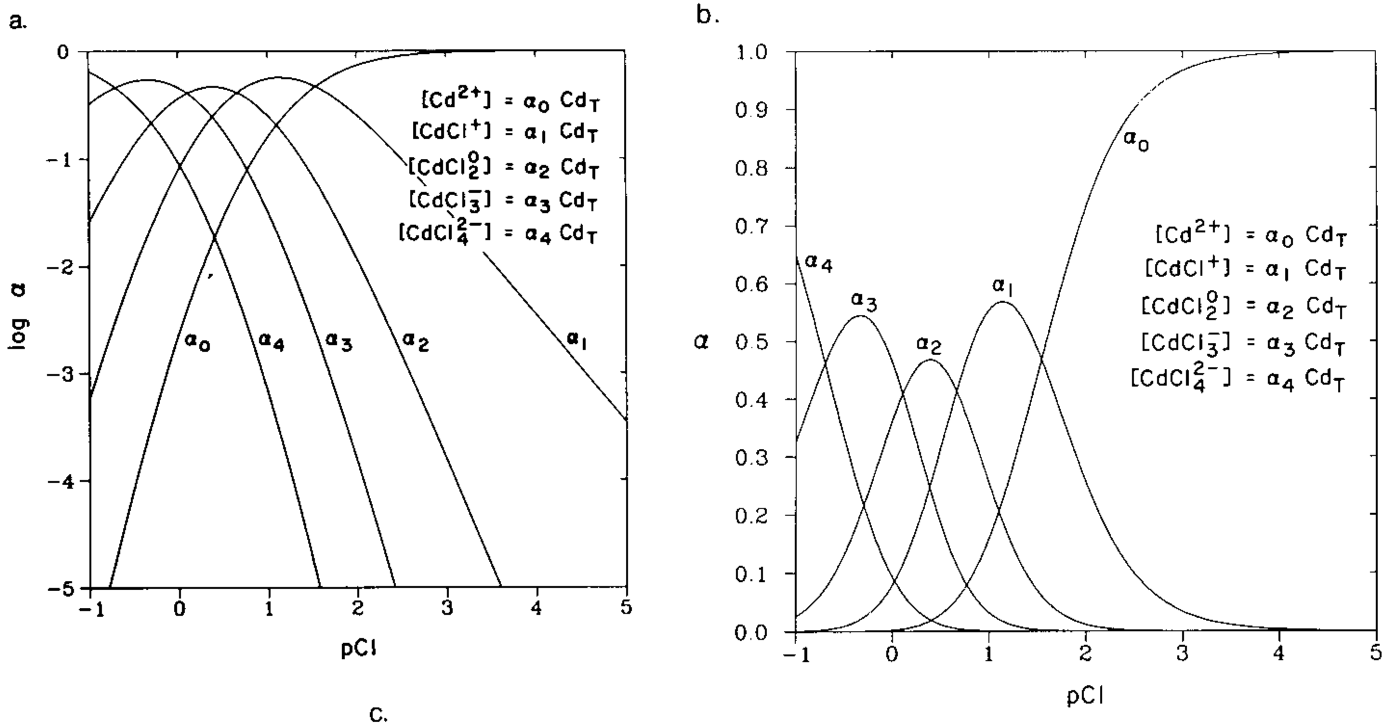


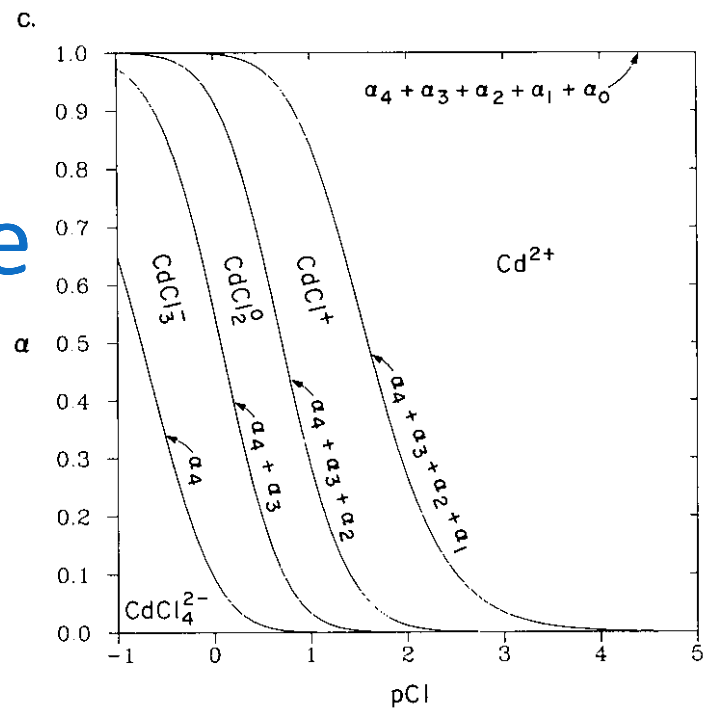
Cadmium Chloride (cont.)



Butler, 1964; pg.269

Cadmium Chloride (cont.)





Pankow, 1991; pg.375

Ligand Number

- Definition
  - The average number of bound ligands per atom of metal
- Significance
  - Defines Mixture
  - Can be analytically determined
    - Used to evaluate β's
  - Can be calculated via 2 independent ways and used to solve problems, if you know the free ligand concentration
    - Mass balance equations
    - Equilibrium equations
  - Thus, we have 2 independent equations and two unknowns (free L, and n-bar), so we can solve

Determination of Ligand

- Equilibrium constant approach

$$\bar{n} \equiv \frac{[ML]+2[ML_2]+3[ML_3]+\cdots+n[ML_n]}{C_M}$$
$$= \frac{[ML]}{C_M}+2\frac{[ML_2]}{C_M}+3\frac{[ML_3]}{C_M}+\cdots+n\frac{[ML_n]}{C_M}$$
$$= \alpha_1+2\alpha_2+3\alpha_3+\cdots+n\alpha_n$$

- And substituting in for the apha's

$$\bar{n} = \alpha_0\beta_1[L]+2\alpha_0\beta_2[L]^2+3\alpha_0\beta_3[L]^3+\cdots+n\alpha_0\beta_n[L]^n$$
$$= \alpha_0\left(\beta_1[L]+2\beta_2[L]^2+3\beta_3[L]^3+\cdots+n\beta_n[L]^n\right)$$

Determination of ligand

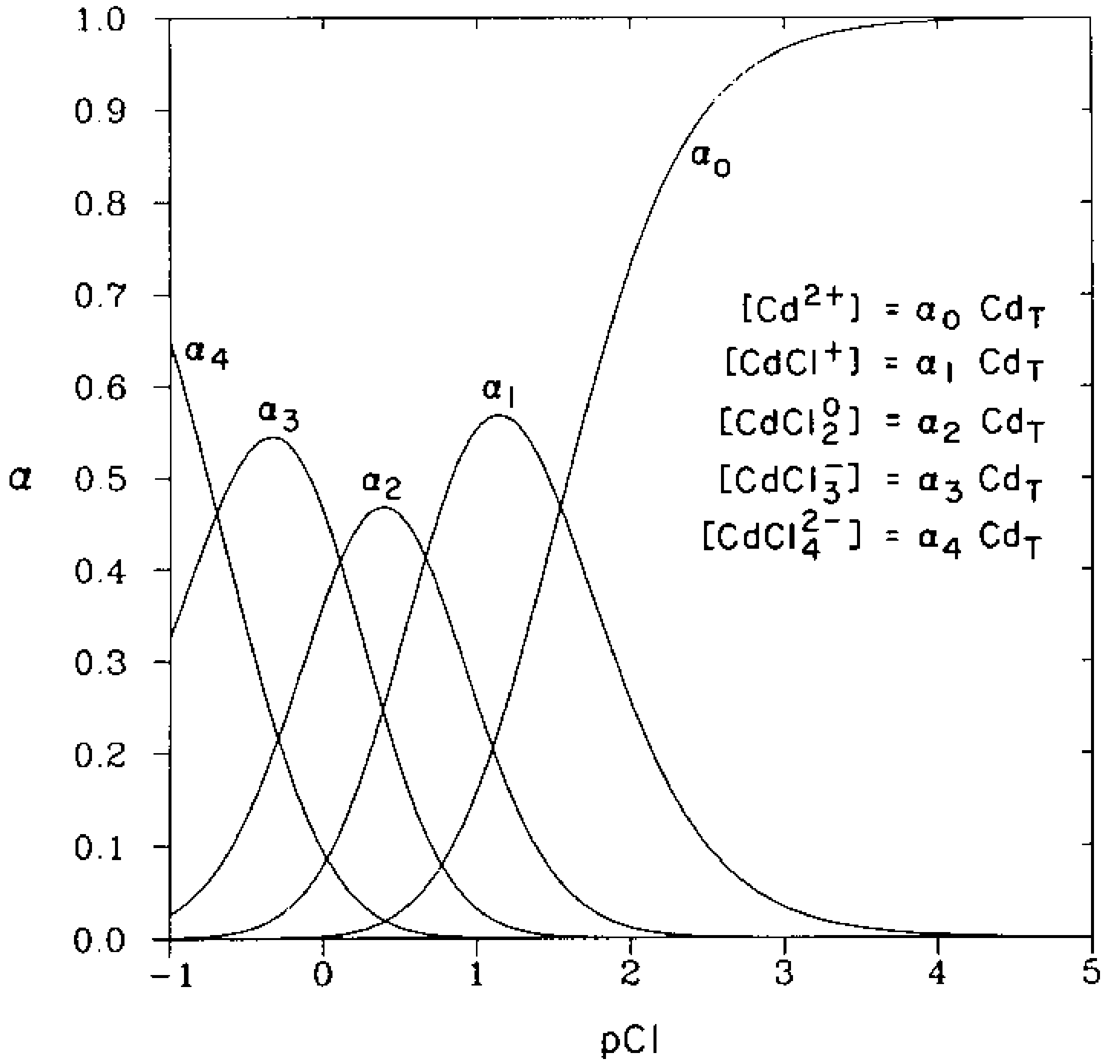
- Mass balance approach
  - $C_M = [M]+[ML]+[ML_2]+[ML_3]+ \quad +[ML_n]$
  - $C_L = [L]+[ML]+2[ML_2]+3[ML_3]+ \quad +n[ML_n]$

$$\bar{n} \equiv \frac{[ML]+2[ML_2]+3[ML_3]+\cdots+n[ML_n]}{C_M}$$

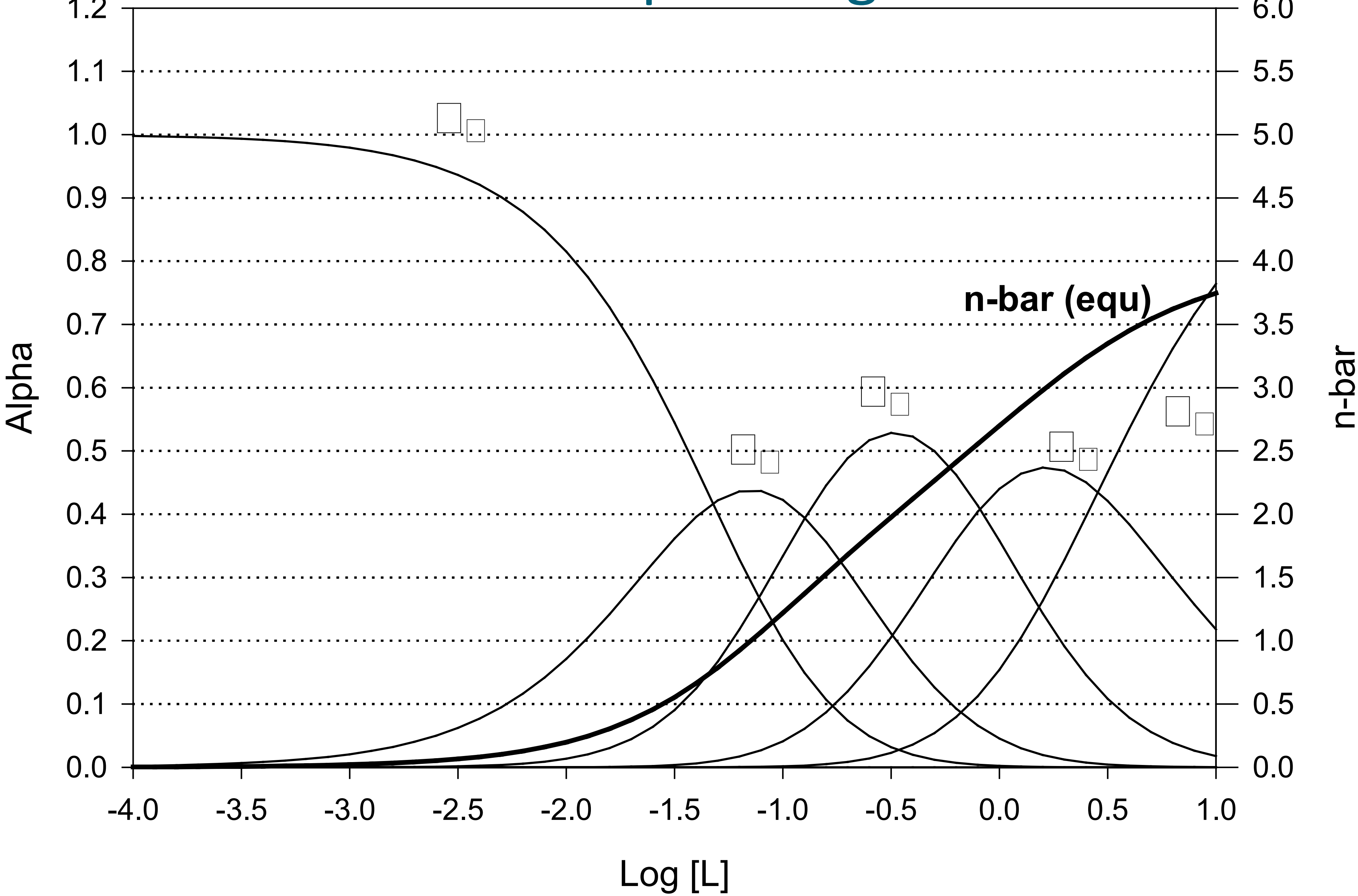
$$= \frac{C_L-[L]}{C_M}$$

Take alpha diagram

- For $CdCl_x$
- Next add n-bar curves
  - One based on equilibria
  - Other based on mass balances



Cadmium Chloride alpha diagram

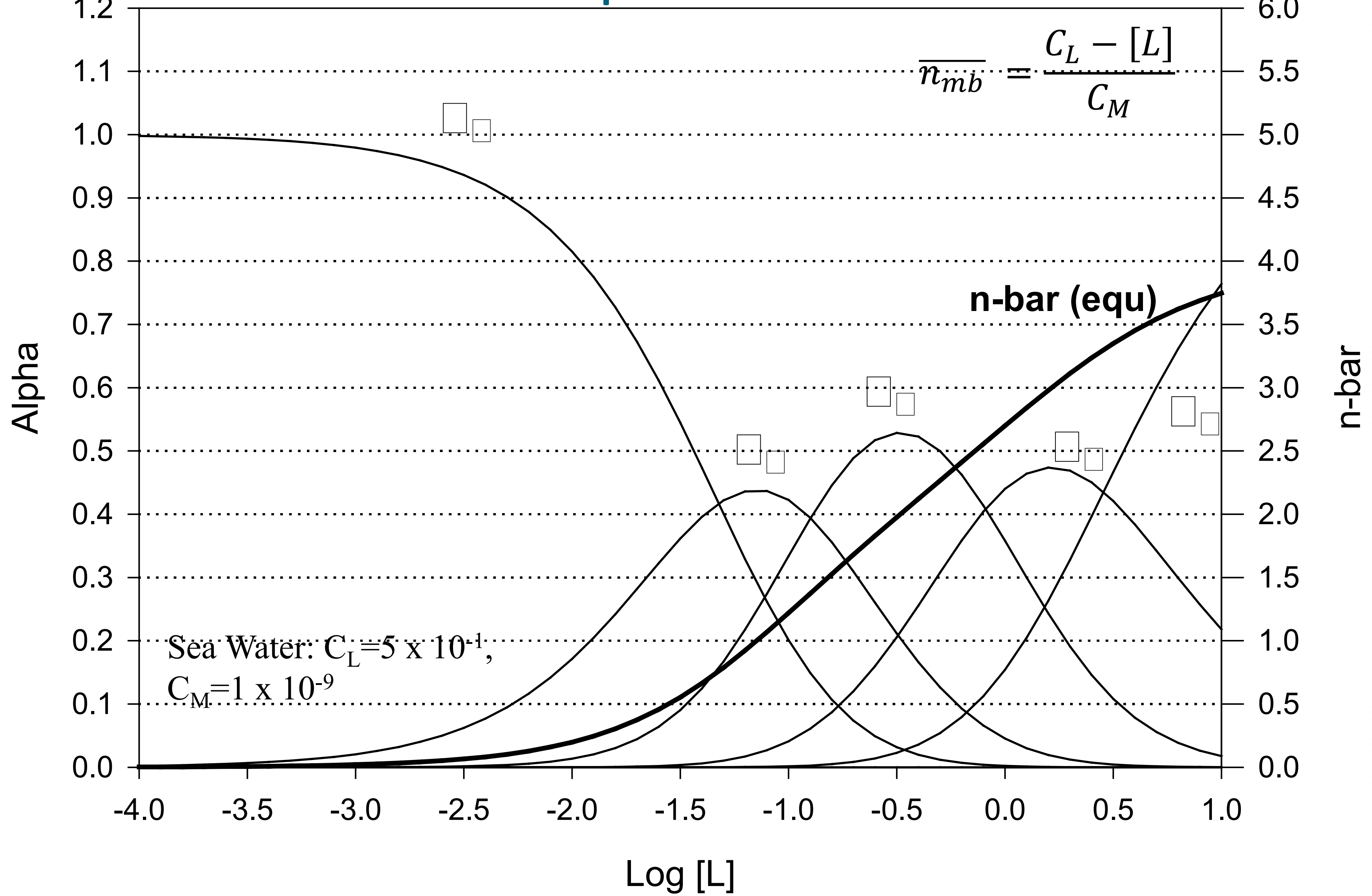


In-Class Problems

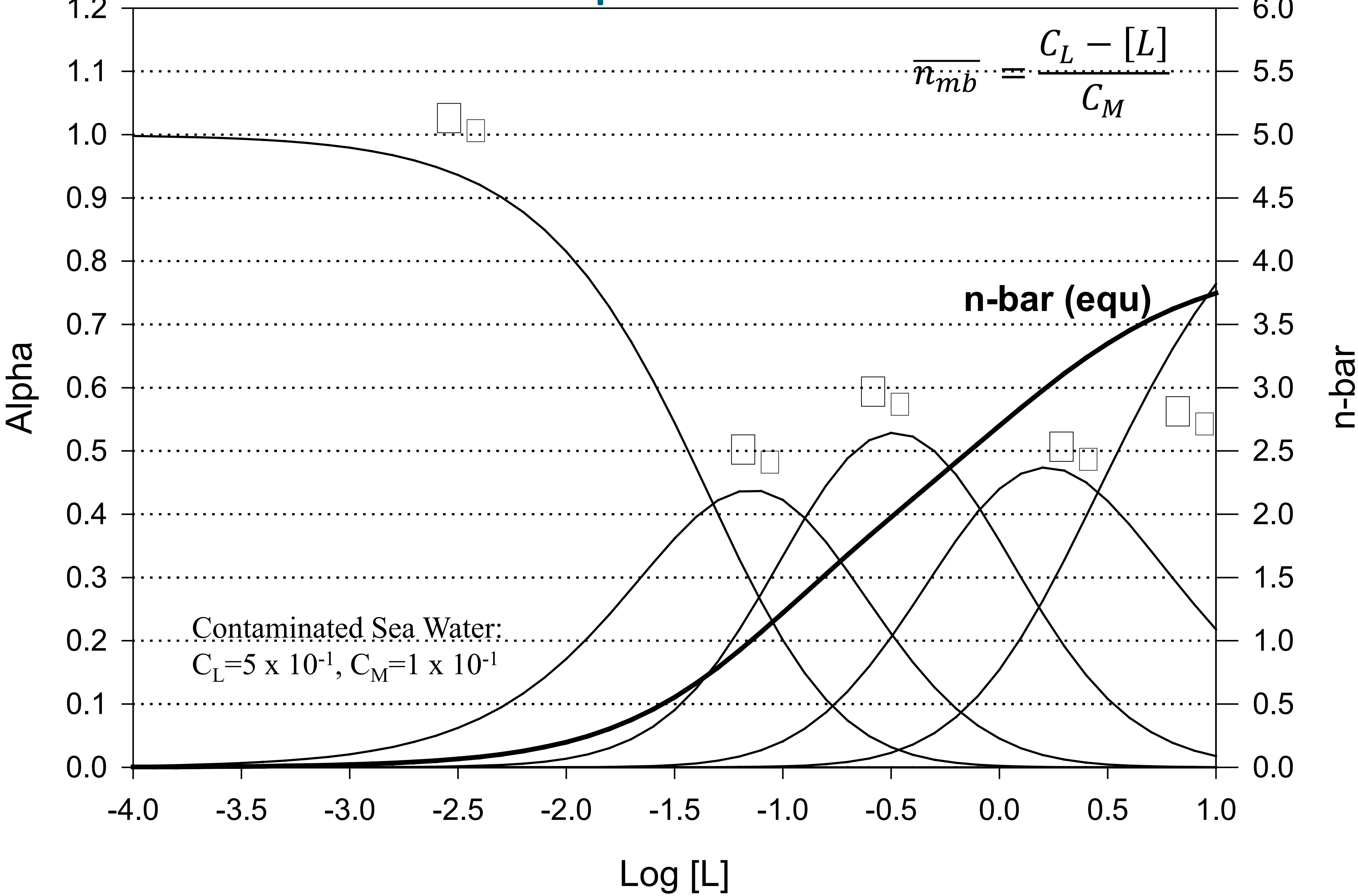
- Class problems with $CdCl_x$
  - Sea Water: C_L=5 x 10^{-1}, C_M=1 x 10^{-9}
  - Contaminated Sea Water: C_L=5 x 10^{-1}, C_M=1 x 10^{-1}
  - Desal Brine: C_L=15 x 10^{-1}, C_M=3 x 10^{-9}
  - RO conc. of Cont. Sea Water: C_L=15 x 10^{-1}, C_M=3 x 10^{-1}

$$\overline{n_{mb}} = \frac{C_L - [L]}{C_M}$$

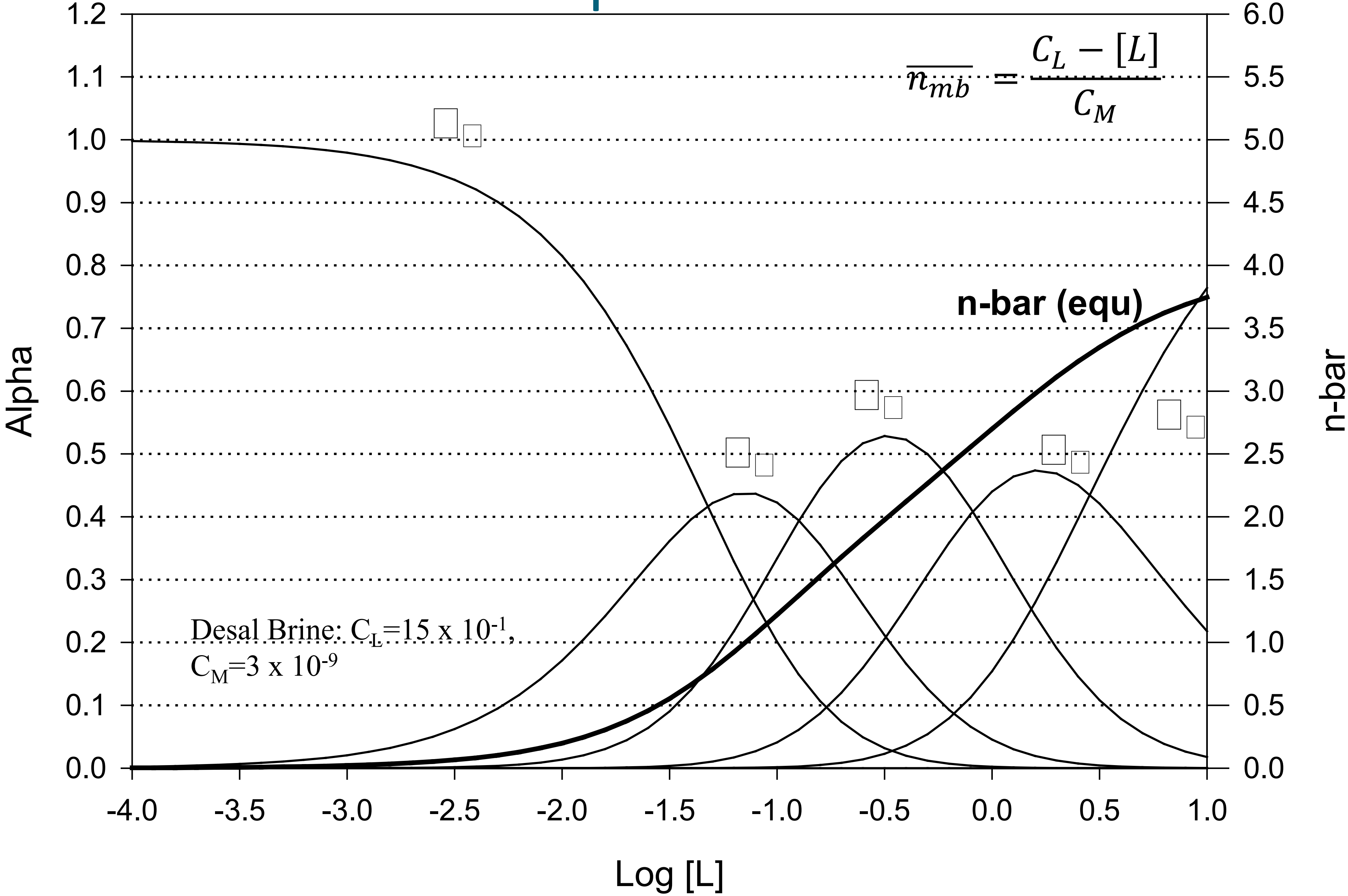
Cadmium Chloride problem



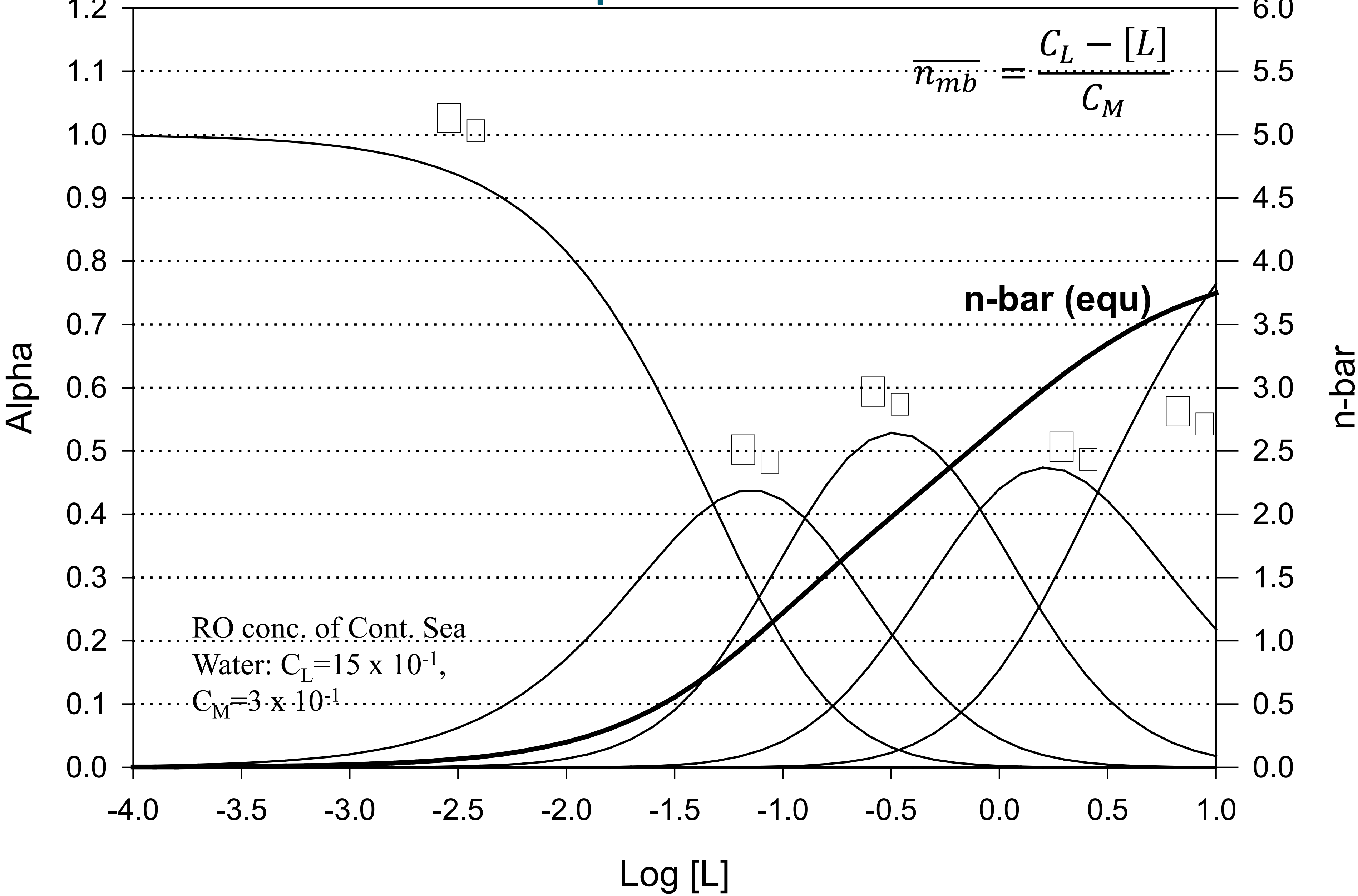
Cadmium Chloride problem 2



Cadmium Chloride problem 3



Cadmium Chloride problem 4



Speciation in Natural Waters

- Mostly Cl complexes in sea water

From: Morel & Malcolm, "*The Biogeochemistry of Cadmium*", Chapt 8 in Metal Ions in Biological Systems, Vol 43 Sigel, Sigel & Sigel, eds.

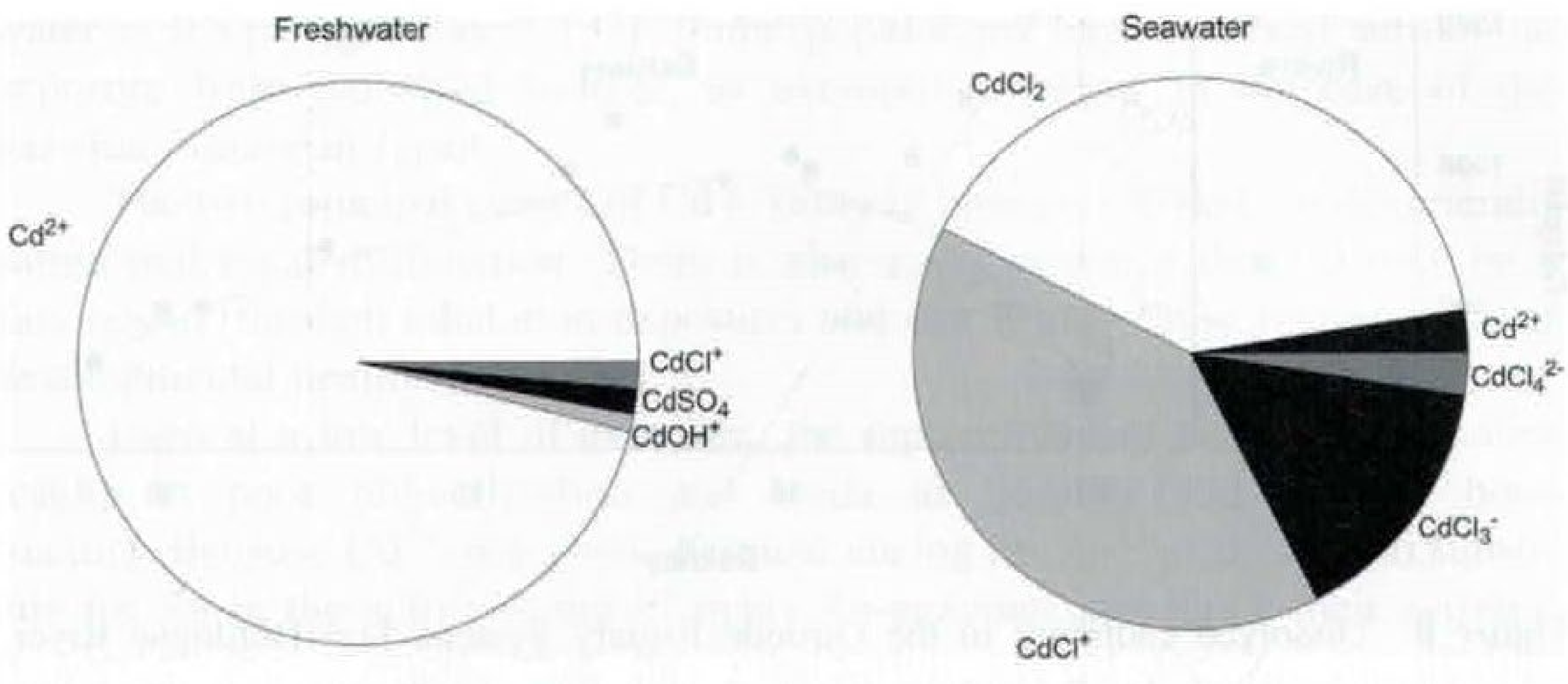
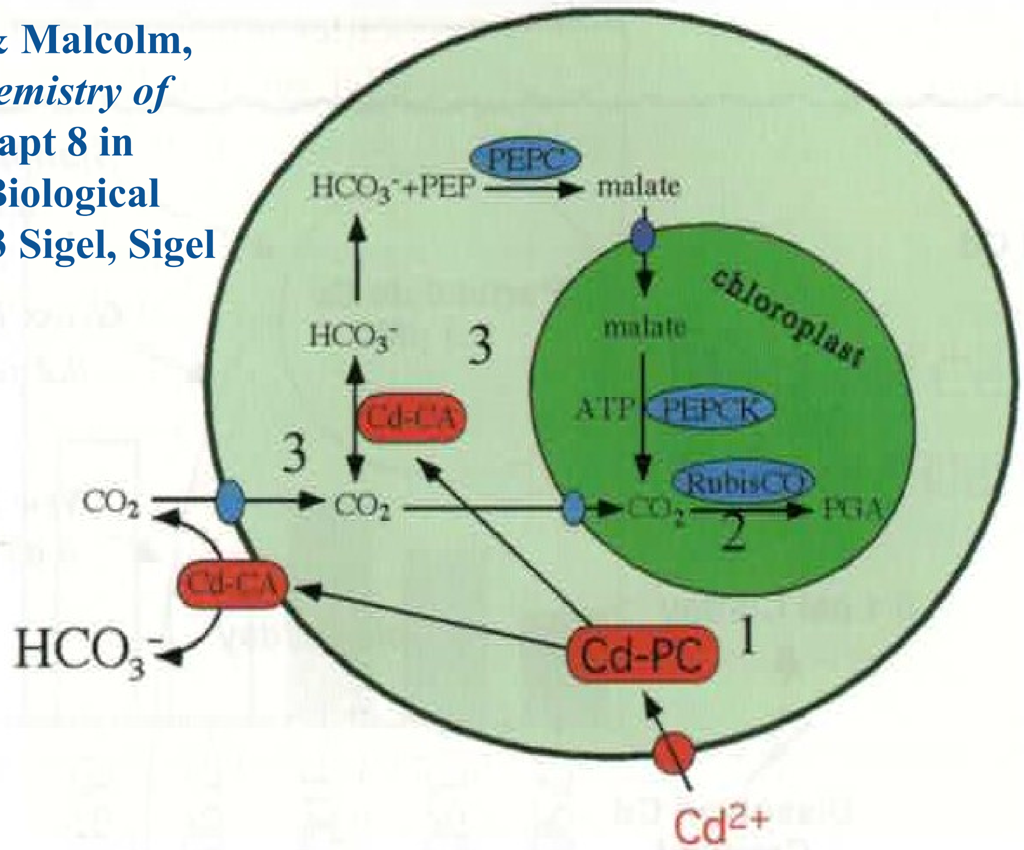


Figure 6 Predicted major chemical species of cadmium in typical freshwater and seawater.

Cellular metabolism of Cd

From: Morel & Malcolm, "*The Biogeochemistry of Cadmium*", Chapt 8 in Metal Ions in Biological Systems, Vol 43 Sigel, Sigel & Sigel, eds.

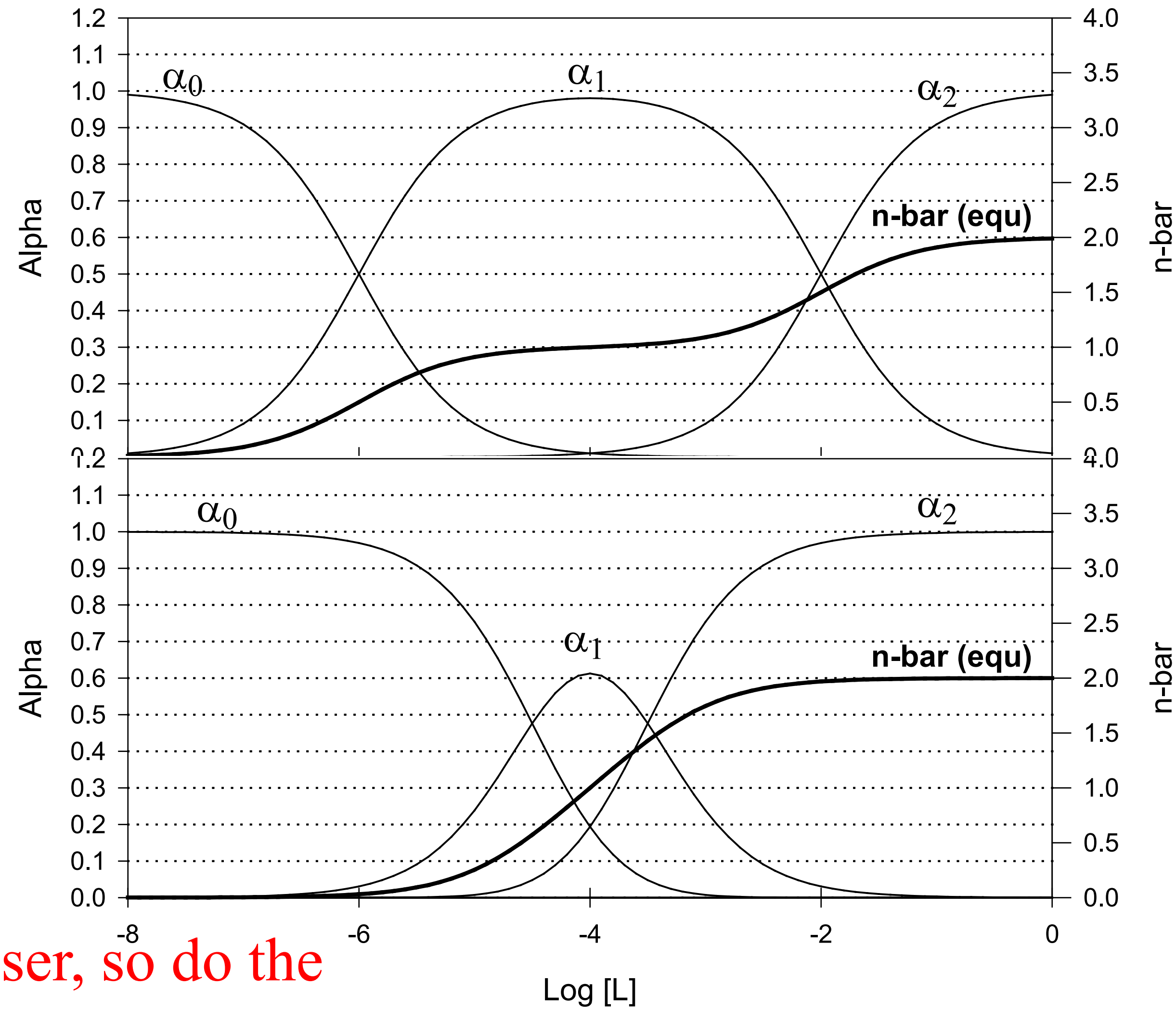


PCs are phytochelatins; metal binding proteins that help regulate Cd concentrations

Figure 13 Hypothetical model of cadmium metabolism in a marine diatom showing the buffering of Cd by PC binding and its use in periplasmic and cytoplasmic carbonic anhydrases as part of C_4 metabolism.

- $K_1=10^6$, $K_2=10^2$

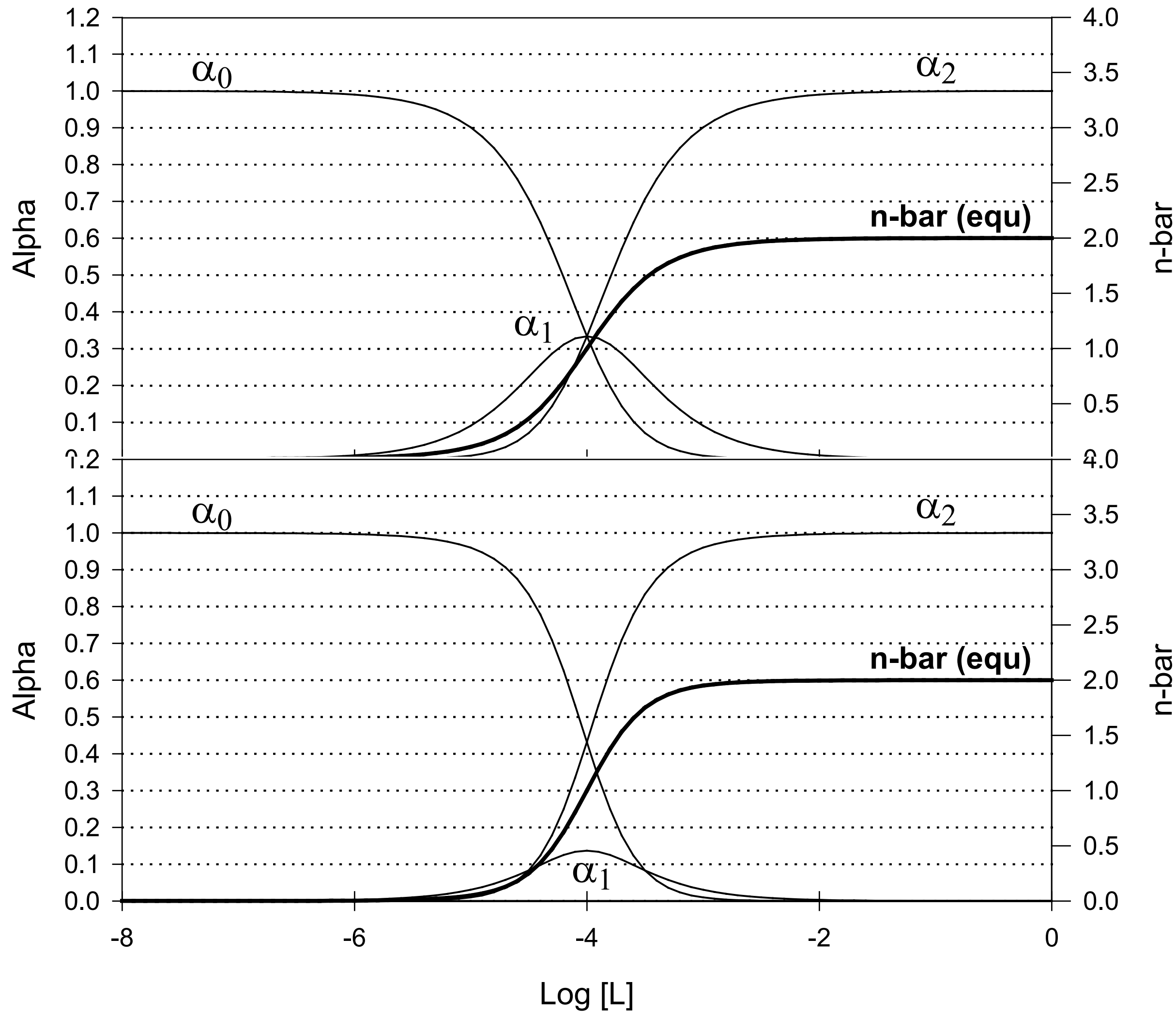
- $K_1=10^{4.5}$, $K_2=10^{3.5}$



Note: as K's get closer, so do the intersections, and the middle alpha's get compressed with diminished height

- $K_1=10^4$, $K_2=10^4$

- $K_1=10^{3.5}$, $K_2=10^{4.5}$



Features of alpha diagrams

- Intersection point for adjacent curves
  - Occur at: log [L] = pK's
    - E.g., first intersection occurs where: $\alpha_o = \alpha_1$ which is where: [M]=[ML]
    - And in general, intersection of adjacent curves will occur where: $[ML_{(i-1)}]=[ML_{(i)}]$
  - So at these intersection points, the metal terms in the equations for K will cancel each other out and:

$$K_i = \frac{[ML_i]}{[ML_{(i-1)}][L]}$$

$$[L] = 1/K_1$$

$$\log[L] = pK_1$$

or

$$K_1 = \frac{[ML]}{[M][L]}$$

$$[L] = 1/K_i$$

$$\log[L] = pK_i$$

Features (cont.)

- An alpha curve will reach its maximum at the point where the preceding alpha and the following alpha intersect (i.e., α_{i-1} and α_{i+1}),
- Consider the intersection of α_{i-1} and α_{i+1}
  - The two K equations are:

$$K_i = \frac{[ML_i]}{[ML_{(i-1)}][L]} \qquad K_{i+1} = \frac{[ML_{i+1}]}{[ML_{(i)}][L]}$$

  - And their product gives us:

$$K_i K_{i+1} = \frac{[ML_{i+1}]}{[ML_{(i-1)}][L]^2}$$

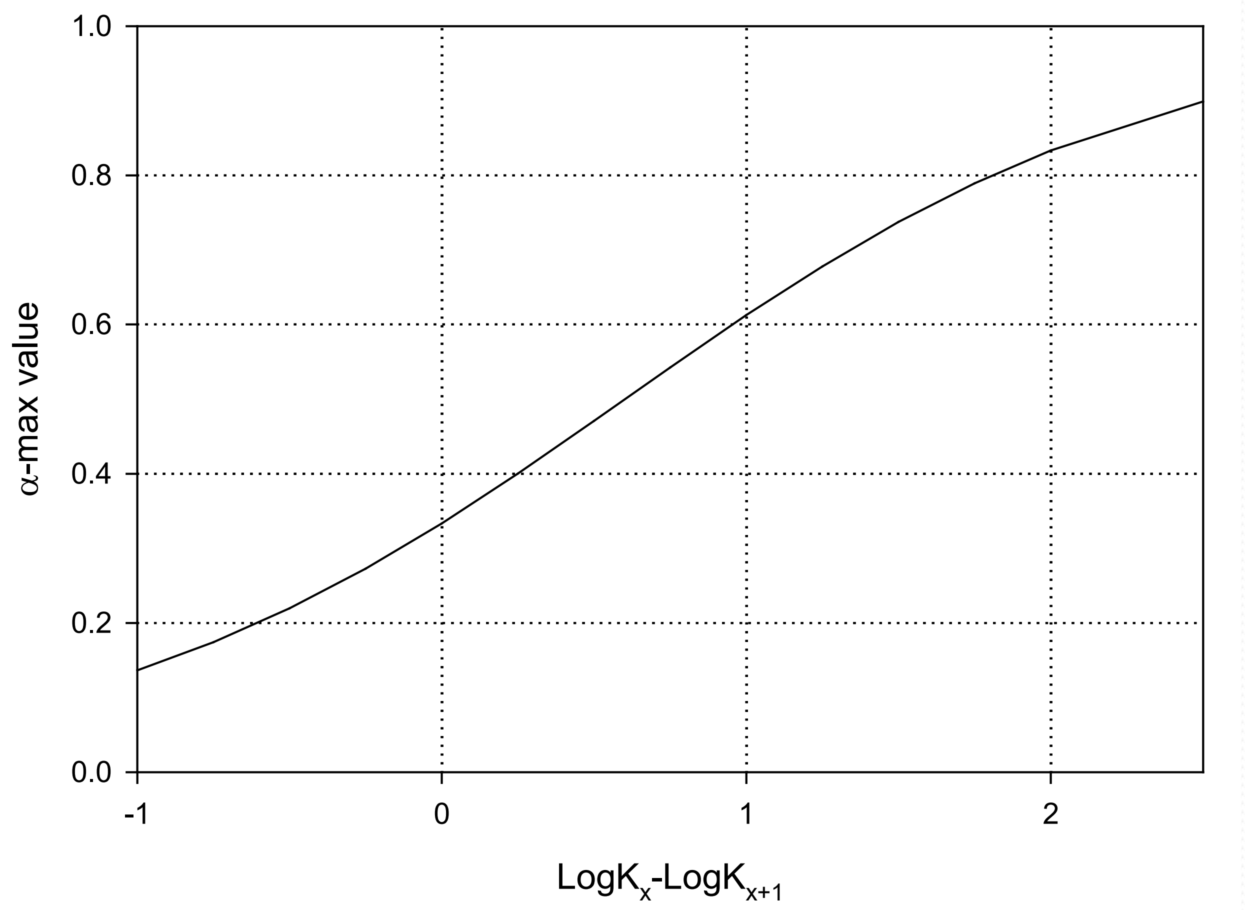
  - Once again, we can cancel metal concentrations to get:

$$[L] = \sqrt{1 / K_i K_{i+1}}$$

$$\log[L] = 0.5(pK_i + pK_{i+1})$$

Height of alpha maximum

- Dependent on difference between K1 and K2



- To next lecture