

SECOND EXAM

Closed book, two pages of notes allowed.

Answer all questions. Please state any additional assumptions you made, and show all work.

1. Carbonate System.

(60% for 1A-D) Two different drinking water supplies are used to provide a total plant flow of 15 MGD. Water #1 is a groundwater that has elevated levels of sulfide. Water #2 is an alkaline surface water. The two are characterized as follows:

Water	Flow (MGD)	Alkalinity (mg/L as CaCO ₃)	pH
#1	10	5	6.50
#2	5	300	8.85

- A. Water #1 is pre-treated with chlorine to oxidize the sulfide to sulfate prior to blending with water #2. If water #1 has a sulfide concentration of 3 mg/L, how much NaOCl must be added to oxidize the sulfide without any extra chlorine left (i.e., no residual chlorine)?

This is just a simple stoichiometry problem, but you have to know what sulfate and sulfide are. You start the problem writing out the reactants and products, and then move on to balancing the equation:



The sodium, chlorine and sulfur are already balanced. For the next step you could look at oxidation states and balance the HOCl/Cl⁻ with the HS⁻/SO₄⁻² that way, but if you're not sure of this, you can simply balance the oxygens by adding more hypochlorite while keeping the chloride and sodium in balance.



Finally you balance the hydrogens by adding H⁺, and check to make sure the charges balance.



Now you've verified that the molar stoichiometry is 4 chlorines per sulfide (or bisulfide). Since sulfide has a GFW of 32 and chlorine is 71 (always expressed as Cl₂), then the required dose is:

$$\begin{aligned}
 \text{Dose} &= 4 \frac{\text{moles - chlorine}}{\text{mole - sulfide}} \times \frac{3 \frac{\text{mg-sulfide}}{\text{L}}}{32000 \frac{\text{mg-sulfide}}{\text{mole-sulfide}}} \times \frac{71000 \text{mg - chlorine}}{\text{mole - chlorine}} \\
 &= \mathbf{26.6} \frac{\text{mg-chlorine}}{\text{L}}
 \end{aligned}$$

B. What is its pH and alkalinity of water #1 immediately after the chlorine and sulfide react?

So for this you need to consider it a closed system. You also need to consider the added or formed alkalinity.

At pH 6.5, its reasonable to assume that all or nearly all of the sulfide is as H₂S, so the net change from the raw water to the chlorinated water is:



$$\frac{\Delta \text{Alk}}{\Delta \text{sulfide}} = \Delta C_B - \Delta C_A = (4 - 0) - (6 - 0) = -2 \frac{\text{eq}}{\text{M}}$$

$$\text{Alk}_f = \text{Alk}_i + \Delta \text{Alk} = \frac{5 \frac{\text{mg}}{\text{L}}}{50 \frac{\text{mg}}{\text{meq}}} - 2 \frac{\text{meq}}{\text{mM}} \left(\frac{3 \frac{\text{mg}}{\text{L}}}{32 \frac{\text{mg}}{\text{mM}}} \right) = -0.0875 \frac{\text{meq}}{\text{L}} = \boxed{-4.375 \frac{\text{mg}}{\text{L}}}$$

So now we calculate the C_T for this water (which does not change with chlorine addition)

$$C_T = \frac{\text{Alk} - [OH^-] + [H^+]}{\alpha_1 + 2\alpha_2}$$

Recall that:

$$\alpha_1 = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}} \quad \alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1}$$

And for pH =6.5, we have:

$$\alpha_1 = 0.585 \quad \alpha_2 = 8.66 \times 10^{-5}$$

$$C_T = \frac{0.1 \times 10^{-3} - 10^{-7.5} + 10^{-6.5}}{0.585 + 2(8.66 \times 10^{-5})} = 0.1712 \times 10^{-3} \text{M}$$

Now we expect that with a drop in alkalinity, the pH will go well below the first pK, and the alpha's can be simplified for the case where pH < pK₁

$$\alpha_1 = \frac{1}{\frac{[H^+]}{K_1}} = \frac{K_1}{[H^+]} \quad \alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1 K_2}} = \frac{K_1 K_2}{[H^+]^2}$$

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

And if we assume that α_2 will be very small

$$C_T = \frac{Alk - \left(\frac{K_W}{[H^+]} \right) + [H^+]}{\left(\frac{K_1}{[H^+]} \right)}$$

$$C_T = Alk \frac{[H^+]}{K_1} + \frac{K_W}{K_1} + \frac{[H^+]^2}{K_1}$$

$$[H^+]^2 + Alk[H^+] + (K_W - C_T K_1) = 0$$

Solving this with the quadratic formula get us:

pH = 4.054

C. What will the pH of the blended water be immediately after mixing?

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
4.054	0.00503	2.66×10^{-9}
8.85	0.9650	0.03195

so, for water #1:

$$C_T = \{(-4.375/50,000) - (10^{-7.50}) + (10^{-6.50})\} / (0.00503 + 2 \cdot 2.66 \times 10^{-9}) = 0.00017 \text{ M}$$

But we didn't have to calculate this again, as it was already determined in part B

and for water #2:

$$C_T = \{(300/50,000) - (10^{-5.15}) + (10^{-8.85})\} / (0.9650 + 2 \cdot 0.03195) = 0.0058246 \text{ M}$$

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

$$\text{Alk} = (10 \cdot (-4.375) + 5 \cdot 300) / 15 / 50,000 = 0.001942 \text{ equ/L}$$

$$C_T = (10 \cdot 0.00017 + 5 \cdot 0.0058246) / 15 = 0.002062 \text{ M}$$

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]

$$C_T = \frac{\text{Alk} - [\text{OH}^-] + [\text{H}^+]}{\alpha_1 + 2\alpha_2}$$

which becomes:

$$C_T \approx \frac{\text{Alk}}{\alpha_1 + 2\alpha_2}$$

$$C_T (\alpha_1 + 2\alpha_2) \approx \text{Alk}$$

$$C_T \left(\frac{1}{\frac{[\text{H}]}{K_1} + 1 + \frac{K_2}{[\text{H}]}} + \frac{2}{\frac{[\text{H}]^2}{K_1 K_2} + \frac{[\text{H}]}{K_2} + 1} \right) \approx \text{Alk}$$

$$C_T \left(\frac{K_1 [\text{H}]}{[\text{H}]^2 + K_1 [\text{H}] + K_1 K_2} + \frac{2K_1 K_2}{[\text{H}]^2 + K_1 [\text{H}] + K_1 K_2} \right) \approx \text{Alk}$$

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

$$C_T K_1 [\text{H}] + C_T 2K_1 K_2 \approx \text{Alk} [\text{H}]^2 + \text{Alk} K_1 [\text{H}] + \text{Alk} K_1 K_2$$

$$\text{Alk} [\text{H}]^2 + (\text{Alk} K_1 - C_T K_1) [\text{H}] + \text{Alk} K_1 K_2 - C_T 2K_1 K_2 \approx 0$$

Now use the quadratic equation:

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

which is simplified to:

$$[H^+] = \frac{-((Alk - C_T)K_1) \pm \sqrt{((Alk - C_T)K_1)^2 - 4Alk((Alk - 2C_T)K_1K_2)}}{2Alk}$$

and $(Alk - C_T)$ is $0.001941 - 0.002062 = -0.0001205$

and $(Alk - 2C_T)$ is $0.001941 - 2(0.002062) = -0.0021826$

$$[H^+] = \frac{5.382 \times 10^{-11} \pm \sqrt{(5.382 \times 10^{-11})^2 - (-3.5417 \times 10^{-22})}}{0.003882}$$

$$[H^+] = 2.854 \times 10^{-8}$$

or

$$\text{pH} = 7.545$$

2. $HCO_3^- \gg CO_3^{2-}$, $\text{pH} \gg \text{p}K_1$ and Alk is large compared to $[OH^-]$ and $[H^+]$

$$C_T = \frac{Alk - [OH^-] + [H^+]}{\alpha_1 + 2\alpha_2}$$

which becomes:

$$C_T \approx \frac{Alk}{\alpha_1}$$

$$C_T(\alpha_1) \approx Alk$$

$$C_T \left(\frac{1}{\frac{[H]}{K_1} + 1 + \frac{K_2}{[H]}} \right) \approx Alk$$

But if $\text{pH} \gg \text{p}K_1$, then we can ignore the first terms in the denominator of the alpha quotient. So this equation simplifies to:

$$C_T \left(\frac{1}{1 + \frac{K_2}{[H]}} \right) \approx Alk$$

$$C_T \left(\frac{[H]}{[H] + K_2} \right) \approx Alk$$

$$C_T[H] \approx Alk[H] + AlkK_2$$

$$(Alk - C_T)[H] + AlkK_2 \approx 0$$

Now we can solve directly for H^+ :

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

$$= 2.77184 \times 10^{-9}$$

or

$$\mathbf{pH = 7.557}$$

or,

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

$$\mathbf{pH = 7.5434}$$

D. What will the pH of the blended water be after it has reached equilibrium with the bulk atmosphere?

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

$$Alk \approx ([HCO_3^-] + 2[CO_3^{2-}])C_T$$

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

$$Alk \approx (\alpha_1 + 2\alpha_2) \left(\frac{K_h p_{CO_2}}{\alpha_0} \right)$$

And now:

$$\frac{Alk}{K_h p_{CO_2}} \approx \left(\frac{\alpha_1}{\alpha_0} + 2 \frac{\alpha_2}{\alpha_0} \right)$$

$$\frac{Alk}{K_h p_{CO_2}} \approx \frac{[HCO_3^-]}{[H_2CO_3]} + 2 \frac{[CO_3^{2-}]}{[H_2CO_3]}$$

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

$$[H^+]^2 - \frac{K_1 K_h P_{CO_2}}{Alk} [H^+] - 2 \frac{K_1 K_2 K_h P_{CO_2}}{Alk} = 0$$

$$[H^+] = \frac{-\left(\frac{K_1 K_h P_{CO_2}}{Alk}\right) \pm \sqrt{\left(\frac{K_1 K_h P_{CO_2}}{Alk}\right)^2 - 4\left(2 \frac{K_1 K_2 K_h P_{CO_2}}{Alk}\right)}}{2}$$

$$= 2.39054 \times 10^{-9}$$

or

$$\mathbf{pH = 8.622}$$

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

Charge balance considerations dictate that:

$$Alk = C_T$$

Under conditions where $pK_1 \ll pH \ll pK_2$, 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:

$$[H_2CO_3^*] = K_H p_{CO_2}$$

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

$$[H^+] = 10^{-11.35} / Alk, \quad \text{which is equivalent to: } [H^+] = \frac{K_H P_{CO_2} K_1}{Alk}$$

and substituting in for the blended water alkalinity

$$[H^+] = 10^{-11.35}/0.001942$$
$$[H^+] = 2.301 \times 10^{-9}$$

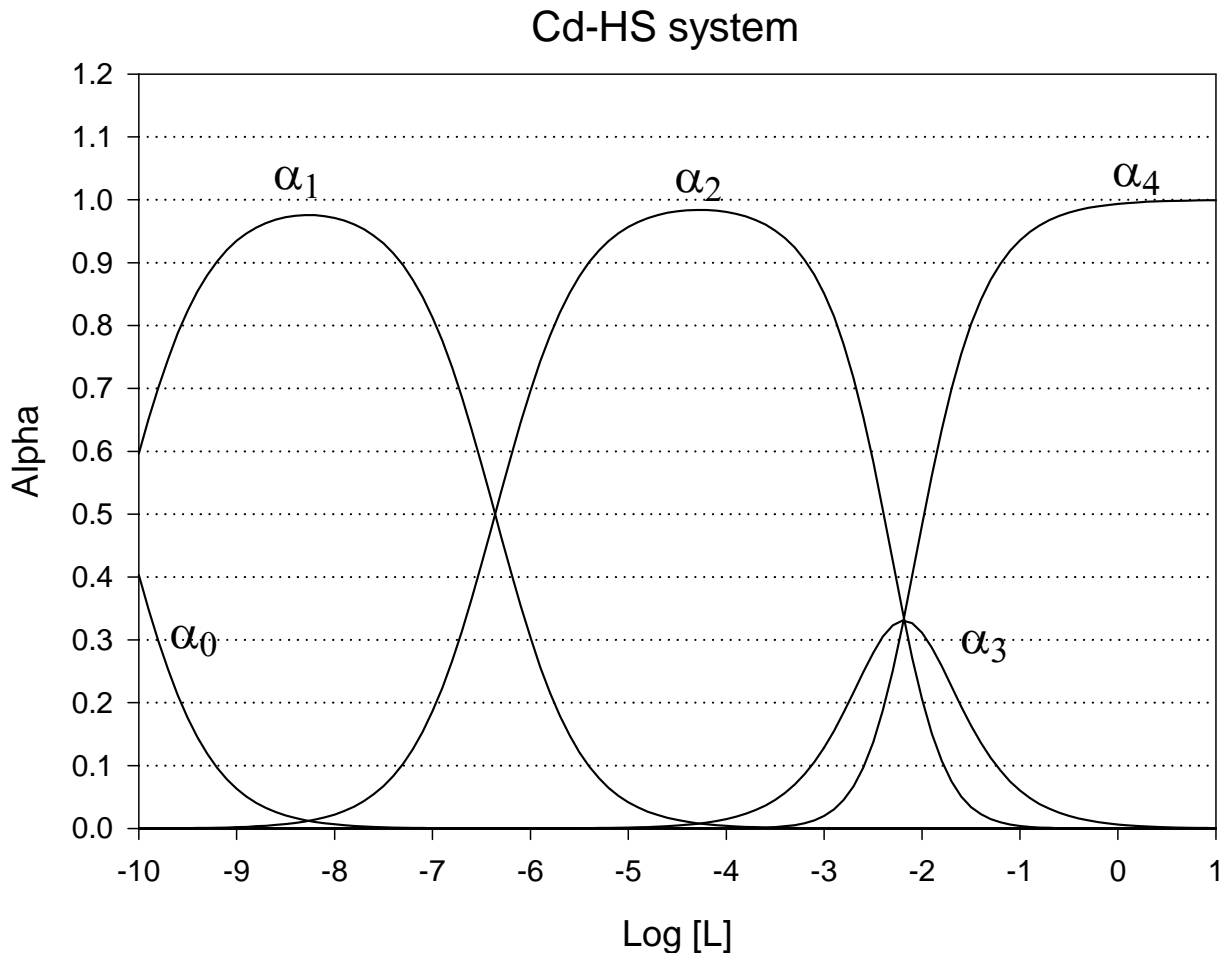
or

$$\text{pH} = 8.638$$

2. Complexation

(40% total for both parts) Bisulfide forms strong complexes with many metals. The following two part problem concerns complexes with Cadmium and Copper.

- A. (20%) Attached is an accurate graph of alpha values (vs $\log[HS^-]$) for the Cadmium-Bisulfide system (equilibria data shown below). Using this graph determine the complete species composition when the total Cadmium concentration is 0.50 mM and the total sulfide concentration is 1.0 mM. Ignore the possible formation of any other complexes other than those from Cd and HS; also ignore any possible precipitation reactions. Assume the water is at neutral pH 9.



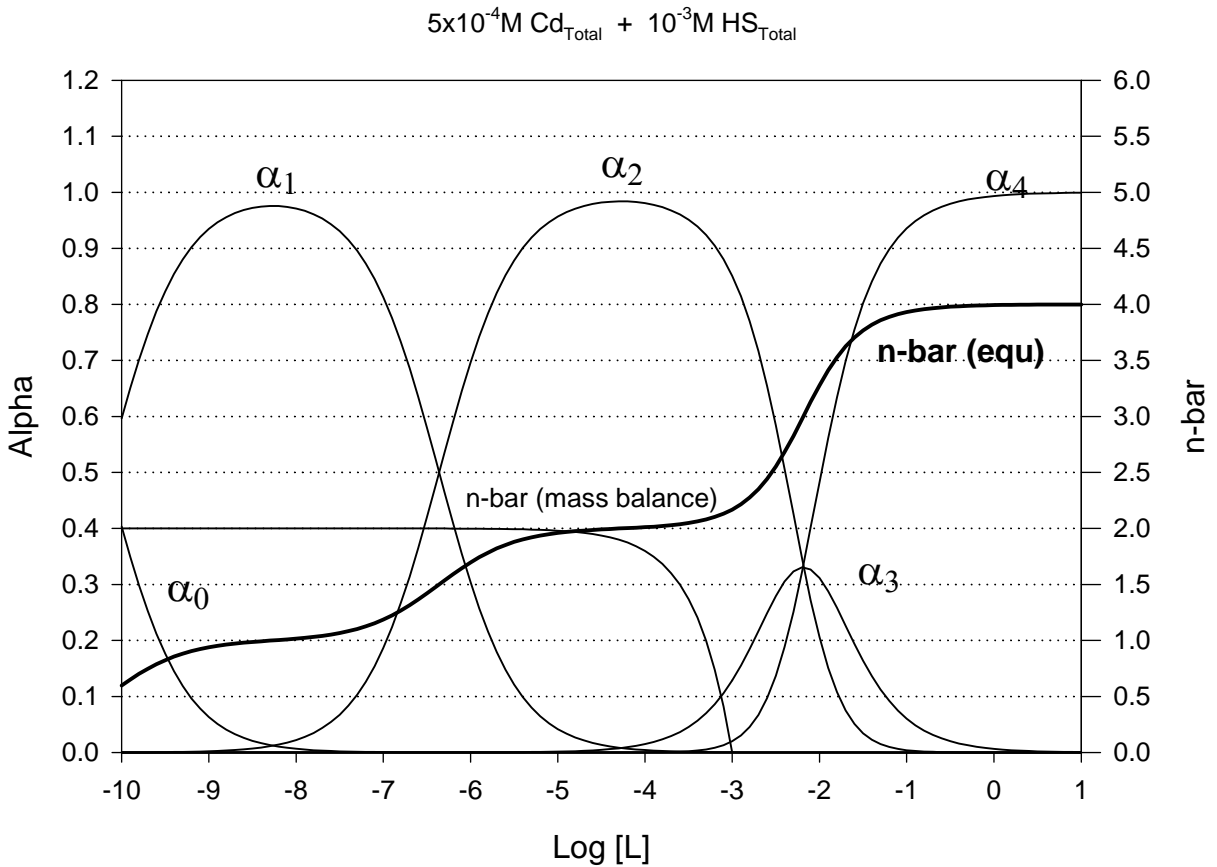
First you draw the n-bar equilibrium curve as practiced in class. Then you determine the mass balance version from the equation:

$$n - \text{bar}(\text{mass balance}) = \frac{L_T - [L]}{Me_T}$$

Which for this example, becomes:

$$n - \text{bar}(\text{mass balance}) = \frac{1 \times 10^{-3} - [L]}{5 \times 10^{-4}}$$

Now plot this curve and find intersection with the n-bar (equilibrium) curve.



Finding the intersection of the two n-bar curves, you can read the alpha values directly from the graph.

The precise values (from calculations) are:

	Log[L]	[L]	alpha 0	alpha 1	alpha 2	alpha 3	alpha 4	n-bar
A	-4.85	1.41254E-05	1.43179E-07	0.0299144	0.968011347	0.002069572	4.528E-06	1.9721639

Then multiplying these alpha values by the total metal concentration, we get the molar concentrations:

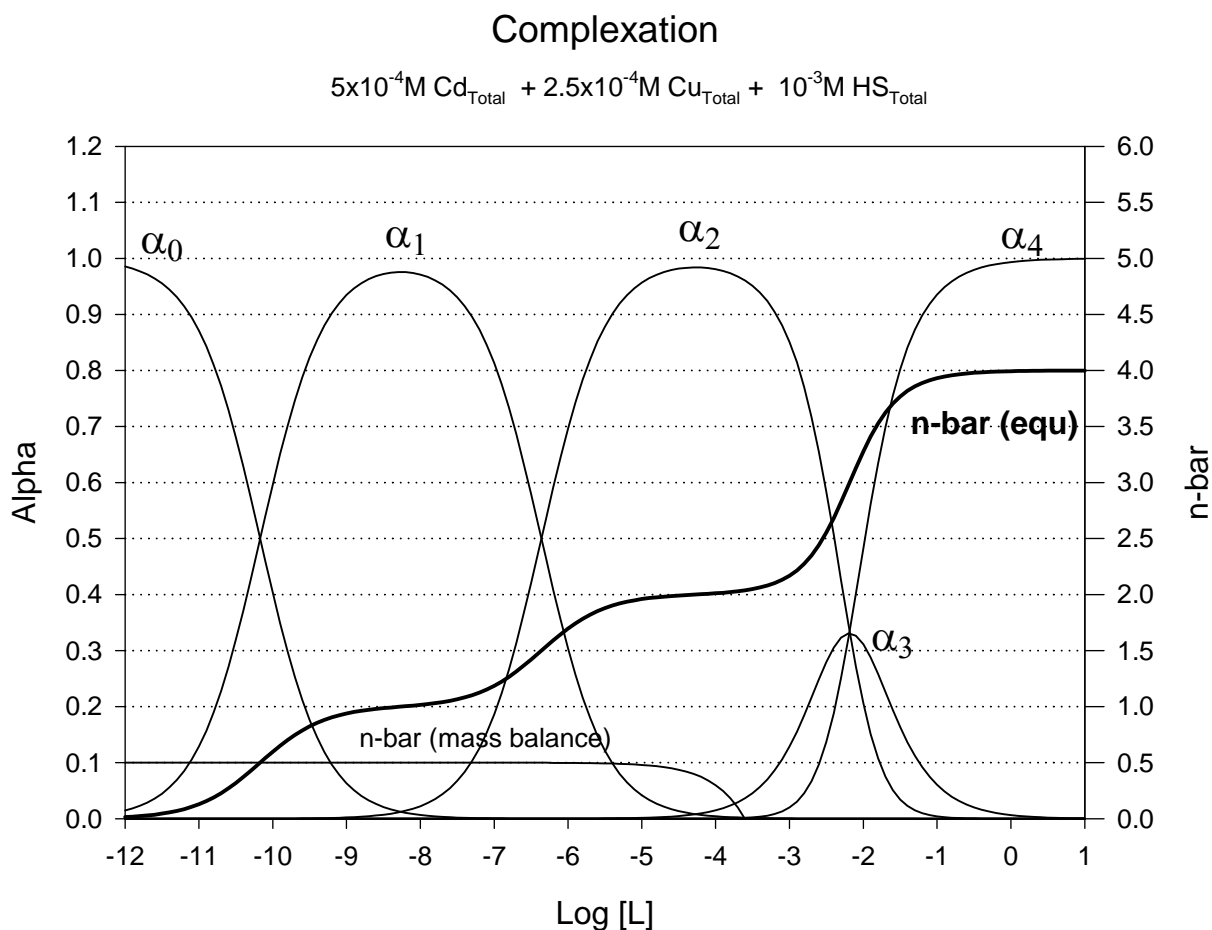
	HS	Cd	CdHS	Cd(HS)2	Cd(HS)3	Cd(HS)4
A	1.413E-05	7.159E-11	1.496E-05	4.840E-04	1.035E-06	2.264E-09

- B. (20%) Your textbook notes that copper forms an especially strong $\text{Cu}(\text{HS})_3^-$ complex with a $\log\beta_3$ equal to 25.9. No other Cu-HS complexes are listed. Based on this information, if you add 0.25 mM total copper to the solution in part A, what will the solution composition be?

In this case, we have a metal (Cu) which will easily out-compete the cadmium for the ligand. This means that you can effectively reduce the total ligand available to the Cd by the amount of Cu added times three (since it forms an MeL_3 complex. So the new n -bar (mass balance) becomes:

$$n\text{-bar}(\text{mass balance}) = \frac{2.5 \times 10^{-4} - [L]}{5 \times 10^{-4}}$$

Now plot this new curve and find intersection with the n -bar (equilibrium) curve. You may choose to extrapolate the curves (as I've done graphically below) as the intersection appears to occur just below 10^{-10} free ligand.



Finding the intersection of the two n-bar curves, you can read the alpha values directly from the graph.

The precise values (from calculations) are:

	Log[L]	[L]	alpha 0	alpha 1	alpha 2	alpha 3	alpha 4	n-bar
B	-10.17	6.7608E-11	4.9996E-01	4.9996E-01	7.7435E-05	7.9239E-13	8.2973E-21	5.0012E-01

Then multiplying these alpha values by the total metal concentration, we get the molar concentrations:

	HS	Cd	CdHS	Cd(HS)2	Cd(HS)3	Cd(HS)4	Cu	Cu(HS)3
B	6.761E-11	2.500E-04	2.500E-04	3.872E-08	3.962E-16	4.149E-24	9.726E-61	2.500E-04

And for Comparison (just FYI, not requested in the problem)

The alpha values are:

	Log[L]	[L]	alpha 0	alpha 1	alpha 2	alpha 3	alpha 4	n-bar
A	-4.85	1.413E-05	1.43179E-07	0.0299	0.9680	0.0021	4.52773E-06	1.97
B	-10.17	6.761E-11	0.499961283	0.5000	0.0001	7.92E-13	8.29729E-21	0.50

The molar concentrations are:

	HS	Cd	CdHS	Cd(HS)2	Cd(HS)3	Cd(HS)4	Cu	Cu(HS)3
A	1.413E-05	7.16E-11	1.50E-05	4.84E-04	1.03E-06	2.26E-09		
B	6.761E-11	2.50E-04	2.50E-04	3.87E-08	3.96E-16	4.15E-24	9.73E-61	2.50E-04

Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

NAME	FORMULA	pK _a
Perchloric acid	$\text{HClO}_4 = \text{H}^+ + \text{ClO}_4^-$	-7 STRONG
Hydrochloric acid	$\text{HCl} = \text{H}^+ + \text{Cl}^-$	-3
Sulfuric acid	$\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$	-3 (&2) ACIDS
Nitric acid	$\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$	-0
Hydronium ion	$\text{H}_3\text{O}^+ = \text{H}^+ + \text{H}_2\text{O}$	0
Trichloroacetic acid	$\text{CCl}_3\text{COOH} = \text{H}^+ + \text{CCl}_3\text{COO}^-$	0.70
Iodic acid	$\text{HIO}_3 = \text{H}^+ + \text{IO}_3^-$	0.8
Bisulfate ion	$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	2
Phosphoric acid	$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$	2.15 (&7.2,12.3)
Citric acid	$\text{C}_3\text{H}_5\text{O}(\text{COOH})_3 = \text{H}^+ + \text{C}_3\text{H}_5\text{O}(\text{COOH})_2\text{COO}^-$	3.14 (&4.77,6.4)
Hydrofluoric acid	$\text{HF} = \text{H}^+ + \text{F}^-$	3.2
Nitrous acid	$\text{HNO}_2 = \text{H}^+ + \text{NO}_2^-$	4.5
Acetic acid	$\text{CH}_3\text{COOH} = \text{H}^+ + \text{CH}_3\text{COO}^-$	4.75
Propionic acid	$\text{C}_2\text{H}_5\text{COOH} = \text{H}^+ + \text{C}_2\text{H}_5\text{COO}^-$	4.87
Carbonic acid	$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	6.35 (&10.33)
Hydrogen sulfide	$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$	7.02 (&13.9)
Dihydrogen phosphate	$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$	7.2
Hypochlorous acid	$\text{HOCl} = \text{H}^+ + \text{OCl}^-$	7.5
Boric acid	$\text{B}(\text{OH})_3 + \text{H}_2\text{O} = \text{H}^+ + \text{B}(\text{OH})_4^-$	9.2 (&12.7,13.8)
Ammonium ion	$\text{NH}_4^+ = \text{H}^+ + \text{NH}_3$	9.24
Hydrocyanic acid	$\text{HCN} = \text{H}^+ + \text{CN}^-$	9.3
Phenol	$\text{C}_6\text{H}_5\text{OH} = \text{H}^+ + \text{C}_6\text{H}_5\text{O}^-$	9.9
m-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COO}^- = \text{H}^+ + \text{C}_6\text{H}_4(\text{O})\text{COO}^{2-}$	9.92
Bicarbonate ion	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	10.33
Monohydrogen phosphate	$\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$	12.3
Bisulfide ion	$\text{HS}^- = \text{H}^+ + \text{S}^{2-}$	13.9
Water	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	14.00
Methane	$\text{CH}_4 = \text{H}^+ + \text{CH}_3^-$	34

