CEE 680 Spring 2020

Water Chemistry

Homework Set #7

Problem #1 **(1 point)**

1. Nickel forms a series of complexes with aqueous ammonia. Draw a set of alpha curves (vs log[NH_3]) for the Nickel Ammonia system. Use the following stability constants (determined from Smith & Martel; Vol.4, pg.40). Include also an n-bar curve.

$\log K_1 = 2.72$

$\log K_2 = 2.17$

$\log K_3 = 1.66$

$\log K_4 = 1.12$

$\log K_5 = 0.67$

$\log K_6 = -0.03$

Solution to #1

I would use a spreadsheet program to develop alpha curves, and plot them using the same spreadsheet or some other graphics software (I used SigmaPlot). Probably the first step is to determine the various overall beta constants:

Constants	Log(Step-wise "K")	Log(Overall "Beta")
1st	2.72	2.72
2nd	2.17	4.89
3rd	1.66	6.55
4th	1.12	7.67
5th	0.67	8.34
6th	-0.03	8.31

Recall from Lecture 27:

$$\beta_m = \prod_{x=1}^{x=m} K_x = \frac{\left[Me(OH)_m^{+(n-m)}\right]}{[Me^{+n}][OH^-]^m}$$

Next we can apply the complexation equations that are based on the beta's and the free ligand concentration.

and

$$\alpha_0 \equiv \frac{[M]}{C_M} = \frac{1}{1+\beta_1[L]+\beta_2[L]^2+\beta_3[L]^3+\beta_4[L]^4+\beta_5[L]^5+\beta_6[L]^6}$$

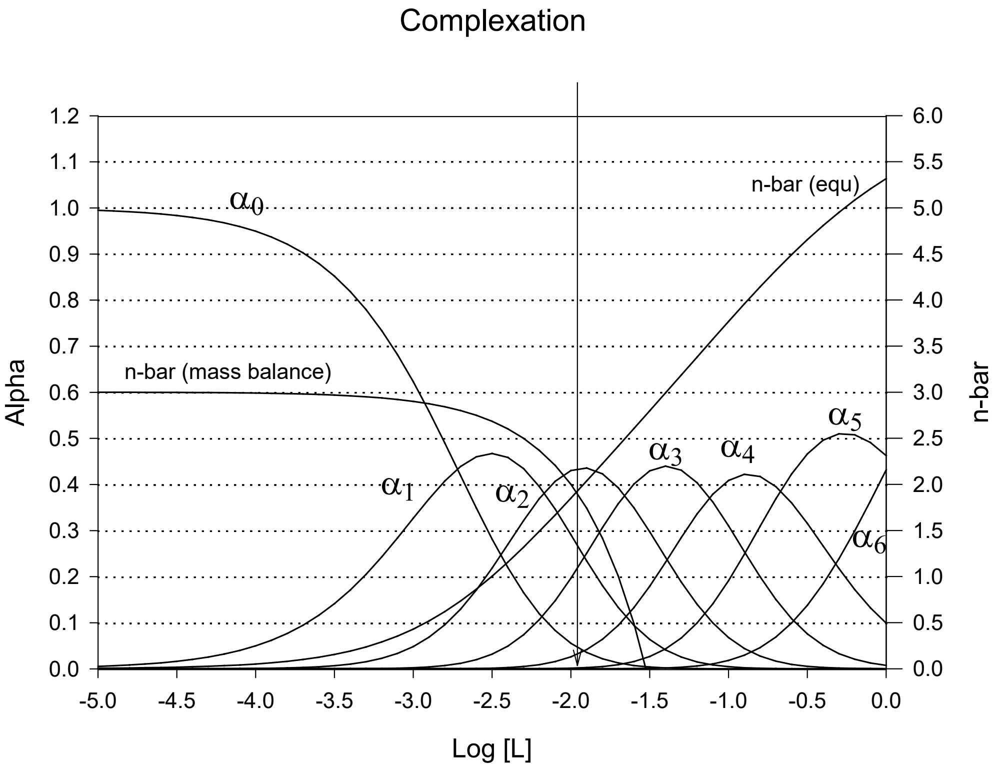
and

$$\alpha_N \equiv \frac{[ML_N]}{C_M} = \alpha_0 \beta_N [L]^N$$

and

$$\bar{n}_{eq} = \alpha_1 + 2\alpha_2 + 3\alpha_3 + 4\alpha_4 + 5\alpha_5 + 6\alpha_6$$

where "M" is Nickel (Ni), and "L" is ammonia (NH_3).



Problem #2 (1 point)

2. Determine the species composition of a solution containing 10 mM total nickel and 30 mM total ammonia. Assume that the solution is buffered at pH 10.3. Then discuss the assumptions you might have made, and how changes in pH might affect this system.

Solution to #2

To solve this specific problem, we need to use the general alpha graph prepared in #1. In addition we have to calculate the mass-balance-based n-bar curve that is specific to these concentration constraints.

$$\bar{n}_{MB} = \frac{C_L - [L]}{C_M}$$

And for this case,

$$\overline{n_{MB}} = 3 - 100[L]$$

This line has been plotted in the graph for problem #1. The intersection with this n-bar curve with the original n-bar curve (the one based only on the equilibrium constants) gives the equilibrium condition. This is indicated by a vertical line. The intersection of this line with all alpha's and with the x-axis gives us the concentration of the various species. Careful inspection of the spreadsheet reveals:

intersection	value	species	concentration (M)
x-axis	-1.965	NH_3	0.0108
alpha-0	0.0476	Ni	4.7E-04
alpha-1	0.2708	$NiNH_3$	2.7E-03
alpha-2	0.4342	$Ni(NH_3)_2$	4.3E-03
alpha-3	0.2151	$Ni(NH_3)_3$	2.2E-03
alpha-4	0.0307	$Ni(NH_3)_4$	3.1E-04
alpha-5	0.00156	$Ni(NH_3)_5$	1.6E-05
alpha-6	1.57E-05	$Ni(NH_3)_6$	1.6E-07

The pH is important, because it will affect the ammonia speciation, and possibly the formation of Nickel hydroxides. Since ammonia has a pKa of 9.3, nearly all of the unbound (by Nickel) ammonia will be in the uncharged form. This is the form that complexes with Nickel. As a result, protonation of ammonia does not appreciably affect the accuracy of our calculations. However, if we had tried to solve this problem for a lower pH, say 8.3, then we would have had to consider the NH_4^+ species explicitly. This becomes a more complex problem, which is probably best solved with a program such as MINEQL. Nevertheless, we can be certain that at lower pH, there would be a lower equilibrium concentration of NH_3, and less complexation of Ni by ammonia. Its also clear that there would be more free Ni as the pH dropped.

Problem #3 (1 point)

3. Using MINEQL prepare a Log Concentration vs pH graph for the copper NTA problem solved in class. But this time assume a total concentration of 10^{-3} M for copper and $10^{-2.7}$ M for NTA. Show the same three species I plotted on my graph, and use the same axis range. Are there differences between your graph and mine? Explain. Prepare a second graph, but this time show other important soluble species and label them.

(Note: for this problem, I would refer you to your earlier notes on MINEQL as well as pages 4-12 through 4-14 in the Version 3.0 MINEQL manual, and similar sections in the v 4.5

manual. Treat this as a pH titration of a system containing Cu and NTA. Note that since we're imposing a pH, it will remain as a Type III species. MINEQL treats a pH variable run as a "titration" where the "logK of pH" is allowed to vary over a fixed range (0-14). Allow MINEQL to form all of the species for which it has equilibrium constants. You may want to save the "Multi", and "S2" files so that you can import them into your favorite graphics or spreadsheet package. I used Sigmaplot.)

Solution #3

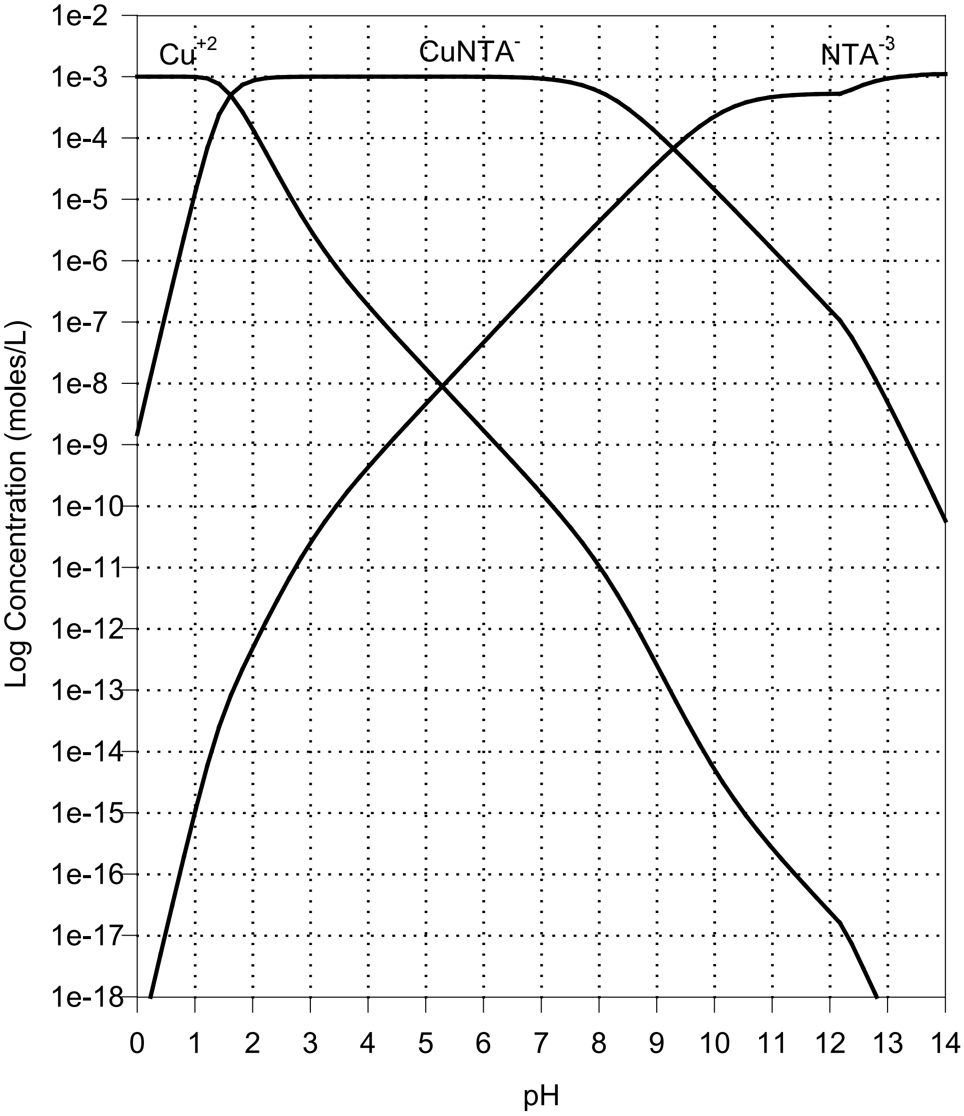
The following graphs are from a "titration" multiple run with MINEQL. The LogK for pH was varied from 0 to 14, with 70 points collected. These were saved and entered into a SigmaPlot file for graphing.

Small differences are evident in comparing these graphs with those presented in class. Evidently, the higher total NTA in this problem depresses the free copper concentration. For example, the copper and copper-NTA lines intersect nearly a pH unit lower with this example. Furthermore, at pH 7, the free copper is about 3 orders of magnitude below where it was in the problem solved in class. This is due to the thousand-fold higher concentration of trivalent NTA at this pH.

In general, all copper species without NTA are depressed in concentration. The copper species with two NTA's is at a substantially elevated concentration.

Another observation is the unusual and changing slopes of many of these lines. This underscores the complexity of a system with so many soluble and insoluble species. Systems with a few species are easy to solve by hand, and easy to visualize. Those with larger numbers of species really require a computer.

Copper & NTA Problem
$Cu_T=10^{-3}$M, $NTA_T=10^{-2.7}$M



Copper & NTA Problem
$Cu_T=10^{-3}M$, $NTA_T=10^{-2.7}M$