Analytical Chemistry
Problem Set 6—due Friday, April 1, 2005 (at 5 p.m.)

Total Points for This Assignment = 65

1. (10 points) Props go out to Emily Kuross, a former Carleton student of mine, for coming up with this first problem. You must use a spreadsheet to solve this problem. Be sure to turn in a copy of it with your work. Up on the mountain of the gods, Cupid is being taught chemistry by Branius Hurtum, the god of science. Right now, Cupid is learning about equilibrium, and Branius realizes that the best way to teach this is from a perspective that the god of love will appreciate and understand. So, for a long period of time he has Cupid observe the relationships of students at Macalester College. At the point when he starts observing the 1800 students on campus, 400 are involved in some sort of amorous relationship; but, by the end of each week, 10% of the people in a relationship have broken it up, while 25% of those not in a relationship have begun a new one. Cupid writes an equation for the "reaction," which looks like this:

\[
2 \text{ single people} \rightleftharpoons 1 \text{ dating couple} \quad (2 \text{ dating people})
\]

a. How many weeks will it take for Macalester to reach "dating equilibrium?"

Note: All numbers in your spreadsheet should be even, since we are assuming that Macalester has an even number of students, and the total number of students dating must be even. Therefore, for each row (week) in your spreadsheet, you should round the number of students breaking up and the number of new dating students to the nearest even number. To implement this in Excel, use this formula: Cell Reference = EVEN (INT (number))

b. At equilibrium, what is the rate of the forward reaction (in people per week)? What is the rate of the reverse reaction? (Round up to whole people, or in case of break-ups, whole couples!)

c. What is the equilibrium constant, \(K_{eq}\), if the activity of people is equal to their dimensionless concentration based on their type (dating vs. single)? Report this value to two significant figures.

d. Cupid notices a nice, single girl who is very sad, for she believes that now that Mac has reached dating equilibrium, she'll never find someone to be with. What should Cupid tell her? Can he quell her fears, or are they well-grounded?

2. (3 points) Harris Problem 9-11

3. (8 points) As part of an effort to make an exotic new fluorescent coating for flat-panel displays, an engineer adds an excess of solid CuCl [copper(I) chloride] and solid TlCl [thallium(I) chloride] to 1.00 ℓ of distilled water.

a. Which of these two salts is more soluble? \(K_{sp}\) values appear in Appendix F.

b. Write the equilibrium expression for the dissolution of each salt.

c. Write the charge balance expression for this solution. Please ignore the dissociation of water, just as Rob did when doing a similar example in class. It is acceptable to ignore \([\text{H}^+]\) and \([\text{OH}^-]\) in this problem because unless there’s another acid or base present, \([\text{H}^+] = [\text{OH}^-]\), and they cancel right out of the charge balance. This is never rigorously true, (in this case Cu\(^+\) can act as an acid, albeit a mighty mighty wimpy one,) but unless one of ions produced is reasonably acidic or basic (SO\(_4^{2-}\), F\(^-\), NH\(_4^+\), and the alkaline earth ions come to mind as examples), it’s a great approximation.

d. Solve this system of three equations and three unknowns to determine \([\text{Cu}^+], [\text{Tl}^+]\), and [Cl\(^-\)]. Note that the extremely low ionic strength makes the activity coefficients essentially unity, and prevents oxidation-reduction reactions from proceeding at an appreciable rate (lest Cu\(^+\) + Tl\(^+\) → Cu\(^0\) + Tl\(^3+\)!)
4. (3 points) Harris Problem 10-17

5. (10 points) Harris Problem 10-20. Also calculate $\alpha_0$ and $\alpha_1$ for HCN in the resulting solution. Note: You must solve this problem using the systematic treatment of equilibrium Rob taught you the week of March 14.

6. (18 points) Harris Problem 11-5. Note: (1) You do not need to employ a systematic treatment of equilibrium to compute these answers; Harris’ approach on p. 211 is fine. However, you are responsible for knowing how one would set up a problem using the more rigorous approach. (2) In your calculations on part (b), you do not need to perform more than one iteration.

7. (10 points) Harris Problem 11-9. Unlike Harris 11-5(b), the point of this problem is precisely to perform multiple iterations. For both parts (a) and (b), you should iterate until two successive calculations of $[\text{HA}^-]$ agree to two significant figures and two successive calculations of pH agree to three significant figures (that is, three decimal places). Be sure to turn in a copy of your spreadsheet.

8. (3 points) Explain briefly why in Problem 7 (Harris 11-9), it was necessary to perform several more iterations to converge the answers to part (b) than to converge the answers to part (a).