Analytical Chemistry
Problem Set 9
Due Friday, May 2, 2008 (at 4:00 p.m.)
Total Number of Points = 57

Note: (1) In computing pH values for Problems 2 and 3 below, you should always use the methods Harris describes in Chapter 11. However, you are responsible for understanding the approximations underlying Harris's approach. Problem #3 does a nice job of demonstrating when Harris's approaches can fail. (2) Report all the pH values you calculate to two decimal places. (3) You do not have to write down explicitly the solution of a quadratic equation with the quadratic formula.

1. (6 points) [Postponed from Problem Set 7] Harris 10-28. Do the calculations at pH 10.00 only.

2. (18 points) (Based on Harris 11-24) A 100.00-mL solution of the diprotic acid H_2A (pK_1 = 4.00; pK_2 = 8.00) was titrated with 1.000 M NaOH. The initial concentration of H_2A is 0.1000 M. Find the pH at the following volumes of base added: 0, 1.00, 10.00, 15.00, 20.00 mL.

3. (13 points) Harris 11-27. Note that the neutral form of the analyte in the problem is called glycine; it is listed in Harris Appendix G. Very briefly state why each of the pH values you compute for part (b) is physically unreasonable.

4. (3 points) Harris 23-7 and 23-8

5. (10 points) Butanoic acid (C_3H_7COOH) shows the following phase equilibrium behavior:

$$C_3H_7COOH(\text{benzene}) \rightleftharpoons C_3H_7COOH(aq) \qquad K = 0.33_3$$

Find the total equilibrium concentration of analyte in each phase when 25 mL of 0.10 M C_3H_7COOH in benzene is extracted by 100. mL of water (a) at pH 4.00 and (b) at pH 10.00. Briefly explain the trend in the concentrations. Warning: Do not use Harris' equation 23-7. Harris always assumes that "phase 2" is the organic phase. I prefer to define "phase 2" as the phase into which the analyte is being extracted.

6. (4 points) The weak base B ($K_b = 1.0 \times 10^{-5}$) really prefers the organic solvent toluene to water:

$$B(\text{toulene}) \rightleftharpoons B(aq) \qquad K = 0.020$$

(a) Using the form of the distribution coefficient we derived in class, calculate *D* at pH 8.00.
(b) Based on the equation for *D*, it is obvious that *D* will be lower at pH 10 than at pH 8. Explain this mathematical prediction qualitatively.

Problem Set 9 continues on the back.

7. (3 points) Harris 23-21. Assume that the solvent has no affinity for the stationary phase. This means that the retention time of the solvent is an accurate estimate of the time required for the mobile phase to travel through the column.

You should also know how to do Harris 23-27, but you do not need to turn in a solution for this problem.