Analytical Chemistry
Problem Set 6—due Friday, March 28, 2008 (at 4:00 p.m.)
Total Number of Points = 63

- Consult Appendix F in your text for any K_{sp} values you need for calculations.
- In activity calculations, carry two additional figures for any intermediate result.
- Please see the attached for a simplified discussion (from the 6th edition of Harris) of how to solve problems with activity coefficients by iteration.

1. (4 points) Harris 8-3

2. (3 points) Harris 8-6(a)

3. (14 points) Harris 8-10. Hint: You should find that a second iteration does not (to two significant figures) change your predicted value of $[Ba^{2+}]$. Briefly explain qualitatively why this is the case.

4. (22 points) Calculate the concentration of dissolved Ca^{2+} in a saturated aqueous solution of $CaSO_4$, taking activity into account. Please note the following:
   - Consider only the reaction
     $$CaSO_4(s) \rightleftharpoons Ca^{2+} + SO_4^{2-} \qquad K_{sp} = 2.4 \times 10^{-5}$$
     (Things could be a whole lot more complicated; see Harris pp. 151-152.)
   - Iterate until two consecutive predictions of $[Ca^{2+}]$ agree to two significant figures.
   - All of your work should be written out for Iteration #1 (which assumes that $[Ca^{2+}] = [SO_4^{2-}] = 0$) and Iteration #2 (which assumes that $[Ca^{2+}]$ and $[SO_4^{2-}]$ are at the concentrations predicted at the end of Iteration #1). You do not need to show your work for the other iterations. You may either write down the key results for each iteration (μ, $\gamma(Ca^{2+})$, $\gamma(SO_4^{2-})$, $[Ca^{2+}]$, and $[SO_4^{2-}]$), or use Excel to calculate and display your results. If you use Excel, be sure to include a copy of your spreadsheet with your problem set.

   [Final answer: $[Ca^{2+}] = 0.0099$ M]

5. (4 points) Harris 8-19. Be sure your Lewis structure includes all lone pairs and non-zero formal charges. You need draw only one resonance structure for $HAsO_4^{2-}$.

6. (5 points) Harris 8-23. Be sure to justify your answer clearly and completely.

7. (11 points) Consider the following (rather simple) problem involving a systematic treatment of equilibrium. To make things even simpler, neglect the effect of activity—that is, assume that all activity coefficients are 1.
   (a) How many moles of PbO will dissolve in 1.00 L of water if the pH is fixed at 10.50? Consider the equilibrium
   $$PbO(s) + H_2O \rightleftharpoons Pb^{2+} + 2\ OH^- \qquad K = 5.0 \times 10^{-16}$$
   (b) Answer the same question asked in (a), but also consider the equilibrium
   $$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+ \qquad K_a = 2.5 \times 10^{-8}$$

   [Final answers: (a) 5.0×10^{-9} mol PbO; (b) 4.0×10^{-6} mol PbO]