CEE 543 Aut 2012 HW#4

1. A wastewater is simulated as an ideal solution containing $10^{-2.7}\,M$ $NaHCO_3$ and $10^{-3}\,M$ NH_4Cl.

   a. Prepare a $\log c$ - pH diagram for the system and use it to determine the pH of the solution. Assume ideal behavior of the solutes.

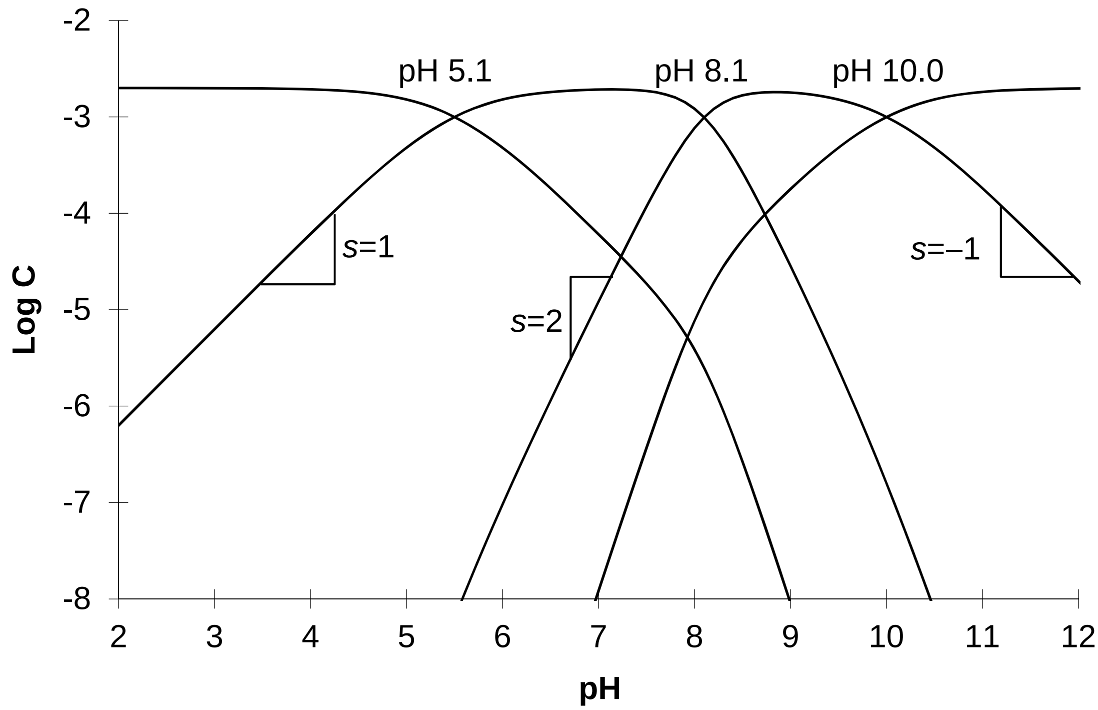
   b. The utility hopes to remove nitrogen from the solution by volatilizing NH_3 gas. To prepare for that step, 148 mg/L $Ca(OH)_2$ (lime) will be added to raise the pH and convert NH_4^+ to the $NH_3(aq)$ form. Calculate the pH after lime addition. (Assume that no $CaCO_3$ precipitation or ammonia loss takes place during lime addition; i.e., all species remain in solution.)

   c. If $CaCO_3$ precipitation did occur during lime addition would it raise, lower, or not change the pH of the solution? (Hint: Consider what species are removed from solution by this reaction, and what the response would be of the species that remain.)

   d. Would removal of $NH_3(aq)$ by volatilization raise, lower, or not change the pH of the solution? Explain your reasoning briefly.

2. Hypobromous acid, HOBr, is an analog of HOCl and participates in many similar reactions, including the reaction with natural organic matter to form halogenated disinfection byproducts. Although HOBr is never added to water as a disinfectant, it can form if ozone (O_3) is used as a disinfectant in water that contains bromide (Br^-) ions. Neither HOBr nor its conjugate base, OBr^-, is included in the default Visual Minteq database. Add OBr^- species to the database for components and HOBr to the database for species, and determine the composition of an ideal solution containing 0.01 M each of NaOBr and NaOCl. Assign values of $a = 3$ and $b = 0$ for the Debye-Huckel parameters for OBr^- in Visual Minteq. [Values for these parameters must be input in the database, but they have no effect on the calculations when the Davies equation (the default option) is used to determine activity coefficients.] Identify which one of the two bases has the greatest effect on solution pH, and explain your reasoning. pK_a for HOBr is 8.63.

3. A $\log c$ - pH diagram for an acid/base system containing $10^{-2.7}\,M$ TOTA is shown below. The fully protonated form of the acid is H_4A. However, the curves are shown for only three species, because one of the potential H_nA species is so unstable that its concentration in this system is always less than $10^{-8}\,M$. The s values indicate the approximate slopes of the curves in the given region, and the pH values indicate the intersection points of the various curves. What is the equilibrium constant for the reaction $H_3A \leftrightarrow HA + 2\,H^+$? What is the value of K_b for a reaction in which HA is the acid?



4. Acid drainage from coal mines can make the receiving waters uninhabitable by fish. To remediate one such situation, a consultant has recommended dissolving limestone, $CaCO_3$, in the drainage water to neutralize the acid. The pH of the untreated water is 2.40 due to the following overall reaction:

$$\mathrm{FeS}(s) + 2.25\ \mathrm{O_2}(aq) + 2.5\ \mathrm{H_2O} \rightarrow \mathrm{Fe(OH)_3}(s) + \mathrm{SO_4^{2-}} + 2\mathrm{H^+}$$

a. Determine is the concentration of $TOT\mathrm{SO_4}$ in the drainage water using manual calculations? Use the Davies equation to model activity coefficients. Is HSO_4^- a strong acid in this solution? (Hint: write out the mathematical expressions that relate the concentrations of H^+, HSO_4^-, and SO_4^{2-} to known values and/or each other. Some of these relationships will include activity coefficients. Then, make a guess for the ionic strength of the solution, compute the activity coefficients, and solve for the species concentrations. Finally, test whether the ionic strength based on those concentrations is consistent with your guess. If not, iterate on the guess until it converges with the computed value.)

b. What is the concentration of Ca^{2+} in the stream after the solution has been neutralized to pH 7.0? Assume that $Fe(OH)_3(s)$ is non-reactive after it precipitates.