CEE 543 Aut 2012 HW#5

1. In the production of metallic objects, the metal parts are often 'pickled' by dipping them in a strong acid to remove surface deposits before the objects are painted or subjected to other surface modification processes. Consider a wastewater from such a process in which steel parts have been dipped in a $0.4\,M$ H_2SO_4 solution. The pH of the wastewater is 0.8. (Note: If you use Visual Minteq to solve this problem, instruct the program to exclude the species $FeSO_4^+$, $Fe(SO_4)_2^-$, $Fe_2(OH)_2^{4+}$, and $Fe_3(OH)_4^{5+}$, using the 'Solid phases and excluded species' menu on the program's main page.)

    a. Assuming that the main effect of the pickling process was to dissolve rust [$Fe(OH)_3(s)$], compute TOTFe in the solution. Consider the acid/base reactions of Fe^{3+} and SO_4^{2-} (given in Table 4.2), and use the Davies equation to estimate activity coefficients.

    b. Compute the amount of lime ($Ca(OH)_2$) needed to bring the solution to pH 5.5 for discharge. Express the result as moles of lime per liter of wastewater. Ignore/ exclude the possible formation of $CaSO_4(aq)$ and any dilution of the original solution by the lime addition. Visual Minteq generates an error message when the ionic strength is $>1\,M$, which is the case at pH 5.5. Therefore, use a fixed ionic strength of $0.9\,M$ for these calculations. (Note: In Visual Minteq, the only species that can be excluded are those that can be formed from the components in the original solution. Therefore, to exclude $CaSO_4(aq)$, you must include Ca^{2+} as a component of that solution, at a negligible concentration.)

2. Colorimetric indicators are convenient for evaluating the pH of a solution within a few tenths of a unit. They are also very useful for indicating the endpoint of a titration. Consider a hypothetical, model indicator "In" which can exist as H_2In^+, HIn^o, or In^-, with $pK_{a1} = 6.0$ and $pK_{a2} = 9.0$. H_2In^+ is red, HIn^o is colorless, and In^- is blue, with the colors becoming noticeable when the solution contains at least $10^{-7}\,M$ of the respective species.

    a. What are the pH and color of a solution made by adding $5\times10^{-7}\,M$ H_2InCl to water?

    b. A solution contains $10^{-3}\,M$ ammonium carbonate, $(NH_4)_2CO_3$, and $5\times10^{-4}\,M$ lime $Ca(OH)_2$. Then, $5\times10^{-7}\,M$ H_2InCl is added. What are the color and pH of the solution?

    c. Nitric acid (HNO_3) is added to the solution in part b until the solution turns red. What is the pH? How much nitric acid was added.? (Hint: Write and solve the TOTH equation for the final condition, using dominant species as reference species and identifying the amount of HNO_3 added as x.)

3. The acid sulfite pulping process uses sulfurous acid (H_2SO_3) to attack the lignin that holds the wood fibers together. The fibers are then released and processed into paper products, and a hot solution containing acetic acid, sulfurous acid, and some larger organic molecules is generated as a waste. This waste solution is partially evaporated and then condensed, with the smaller molecules being transferred into the evaporator condensate and the larger ones remaining behind in an organic-rich solution that can be burned to recover its energy content. The condensate can

be treated in an anaerobic biological treatment process, but only if the pH is maintained near neutrality (pH 7). When the process is operating successfully, the microorganisms mediate the following reactions:

$$CH_3COOH \leftrightarrow CH_4 + CO_2$$

$$4\ H_2SO_3 + 3\ CH_3COOH \leftrightarrow 4\ H_2S + 6\ H_2CO_3$$
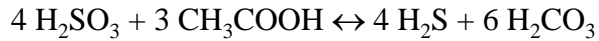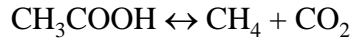
In a well-operating treatment system, essentially all the acetic acid is consumed by the microorganisms, but only a portion of the sulfurous acid is reduced to hydrogen sulfide (at least, that's the empirical result). On a mass basis, the first reaction above dominates, but this might not be the case for the acid/base balance of the solution.

a. Find the pH of a solution of 5000 mg/L HAc and 300 mg/L H_2SO_3-S.

b. What would the solution pH be if all the HAc and all the H_2SO_3 could be destroyed according to the above reactions?

c. How much NaOH, in mol/L, would be needed to bring the pH of the initial solution (as characterized in part a) to 7.0? How much Na_2CO_3 would be required to accomplish the same result? Comment on the relative requirements of these two bases, considering their relative strengths and the number of protons each can accept.

d. If the solution pH were increased to 7.0 with Na_2CO_3 and the biological reaction then proceeded to destroy one-half of the sulfite and all the acetate according to the reactions shown, what would the final pH be?