

CEE 543 Aut 2012 HW#7

- Thiosulfate ion, $S_2O_3^{2-}$, is a complexing agent used extensively in industry. Use Visual Minteq to prepare a $\log c - \log(S_2O_3^{2-})$ diagram showing silver speciation in systems containing $10^{-5} M$ *TOTAg* at pH 9.0 and pH 13.0, over the range $-12 < \log(S_2O_3^{2-}) < -3$. Ignore possible precipitation of solids, and show all species that are present at concentrations $> 10^{-12} M$. Assume all solutes behave ideally.
 - What are the values of $(S_2O_3^{2-})$ at the points where $(Ag^+) = (AgS_2O_3^-)$ and where $(Ag^+) = Ag(S_2O_3)_2^{3-}$, for the system at pH 9? What are the corresponding values at pH 13? Explain this result briefly.
 - The species $AgS_2O_3^-$ should be dominant over a range of values of $(S_2O_3^{2-})$ in the graph at each pH. Explain briefly why the region of $AgS_2O_3^-$ dominance covers a smaller range of $(S_2O_3^{2-})$ at pH 13 than at pH 9.
 - A solution buffered at pH 9 and containing $10^{-5} M$ *TOTAg* is titrated with $S_2O_3^{2-}$. Plot the concentration of S_2O_3 -complexed Ag (i.e., the sum of the concentrations of all $Ag(S_2O_3)_x^{1-2x}$ complexes) as *TOTS* $_2O_3$ is increased from 0 to $10^{-5} M$. What are the concentrations of all species at the end of the titration, i.e., when $TOTAg = TOTS_2O_3 = 10^{-5} M$? Based on this result, is thiosulfate a relatively strong or weak complexing agent for silver? Explain your reasoning.
- A monument made of calcite ($CaCO_3(s)$) has been exposed to the weathering action of the CO_2 of the atmosphere over a period of >2500 years. Starting around 1950, the rate of weathering drastically increased, primarily as a result of the elevated SO_2 content of the atmosphere from the burning of fossil fuels.

Assume that rainfall and P_{CO_2} have been constant over the years at 40 cm/yr and $10^{-3.5}$ atm, respectively, and that the SO_2 content of the atmosphere has been 1 ppm (by volume) since 1950. Calculate the maximum possible extent of weathering (dissolution of $CaCO_3$) for the 2500 years preceding 1950, and for the period 1950 to 2010. Express the results as grams of $CaCO_3(s)$ dissolved per cm^2 cross-sectional area of the monument. Carry out the calculations based on two sets of assumptions. First, assume that the rain is in equilibrium with the atmosphere before striking the monument, but that no more gases dissolve as it drips down the monument's surface. Second, assume that the rain is in continuous equilibrium with the air as it drips. For these simulations, instruct Visual Minteq to exclude consideration of $CaSO_3^0$ and $S_2O_5^{2-}$, and allow the program to account for non-ideal solute behavior. (Note: Visual Minteq might fail to converge in some cases where calcite is input as an infinite solid. If that occurs, try inputting calcite as a finite solid with an initial concentration of 1 mol/L. If the output indicates that some calcite remains at equilibrium, then the solution will be in

equilibrium with that solid and therefore will have the same composition as if it were in equilibrium with an 'infinite' amount of solid.)

3. "pHistory of water". If you solve this problem using Visual Minteq, allow the program to compute ionic strength and adjust for non-ideal solute behavior.
 - (a) A raindrop is formed in a cloud passes over a smokestack and absorbs $10^{-5} M$ H_2SO_4 . Find the solution pH, assuming the droplet equilibrates rapidly with atmospheric CO_2 .
 - (b) The droplet next passes over a feedlot and comes to equilibrium with $P_{NH_3} = 10^{-10.2}$ atm while remaining in equilibrium with CO_2 . Find the new pH and the total dissolved N.
 - (c) Finally, the droplet falls to earth where it hits and starts dissolving a rock containing amorphous silica [$SiO_2(am.ppt)$, $pK = 2.74$ for the reaction $SiO_2(s) + H_2O \leftrightarrow H_4SiO_4$]. The reaction takes place rapidly enough that re-equilibration with the atmosphere does not occur. Prepare a log c – pH diagram for the solution (droplet) at this point, covering the pH range 3 to 12 and showing all species that are present at concentrations $>10^{-12} M$. Find the pH of the droplet and the values of $TOTCO_3$, $TOTN$, and $TOTSi$ at equilibrium.