ENV 6002: Physical & Chemical Principles of Environmental Engineering

Fall 2021 — University of South Florida
Homework #6 — Civil & Environmental Engineering
Due Tuesday, Oct. 19, 2021 — J.A. Cunningham

Assignment for 2021: Problems 1–4, 6, and 7. Skip #5. Each one is worth 16 points. I'll give you the last 4 points if you submit the assignment at the *start* of class.

1. *based on a problem I got from Prof Q Zhang:* During treatment of drinking water, hypochlorous acid (HOCl) is added as a disinfectant. Actually, we typically add Cl_2 (*g*), but when the Cl_2 (*g*) dissolves in water, it is rapidly converted to HOCl, which is a good disinfectant. In fact, HOCl is a much stronger disinfecting agent than its conjugate base, the hypochlorite ion, OCl^-.

   $$HOCl \leftrightarrow H^+ + OCl^- \qquad pK_A = 7.52$$

   If 2.0×10^{-4} moles of HOCl is added to 1.0 L of buffered (pH 8.0) water at 25°C, what is the concentration of the HOCl species once the system has reached equilibrium? What is the concentration of OCl^-? Hint: assume that chemical activity can be approximated by molar concentration.

2. I saw someplace that the standard free energy of formation for H^+ (*aq*) is 0.0 kJ/mol at 25 °C. That surprised me. I wondered how to figure out if it is correct, and I thought of a way we can check it. We know that water dissociates into H^+ (*aq*) and OH^- (*aq*), and we know the equilibrium constant for that dissociation is 1.0×10^{-14} at 25 C.

   $$H_2O\ (lq) \leftrightarrow H^+\ (aq) + OH^-\ (aq) \qquad K = 1.0\times10^{-14}$$

   Using this equilibrium, along with Table 5-6 in your text book, estimate/calculate the standard free energy of formation, $\Delta G_f°$, for H^+ (*aq*). Is it 0 kJ/mol as I had read?

3. *based on a problem I got from Prof Q Zhang*: Let's think some more about our HOCl disinfectant from problem 1. HOCl can decompose according to the following reaction.

   $$2\ HOCl\ (aq) \leftrightarrow 2\ Cl^- + 2\ H^+ + O_2\ (aq)$$

   We want to determine how much HOCl decomposition we will suffer under typical water-treatment conditions. Hopefully not very much.

   a. Determine the equilibrium constant for the given reaction at 25 C. Use $\Delta G_f°$ values from your text book, along with your finding from problem 2. Make sure to use the aqueous form of O_2. Also, your book writes HOCl as HClO – it's the same thing.

problem 3 continues →

3. continued

   b. Suppose we have added HOCl to water such that we have the following concentrations. HOCl = 7.1 mg/L as Cl_2, pH = 7, O_2 (*aq*) = 6.4 mg/L, and Cl^- = 10^{-3} M. Determine if HOCl is thermodynamically stable in water under these conditions. The temperature is 25 °C. Assume that chemical activity can be approximated by molar concentrations for all species involved.

   c. If HOCl decomposes under the conditions given in part (b), what is the maximum conversion of HOCl? Does most of it dissociate, or does most of it remain as HOCl? Assume that the concentration of H^+ remains constant as HOCl dissociates, but the concentration of Cl^- and O_2 can change. Hint: you can write the concentrations of each chemical in terms of the extent of reaction, ε. Then you can find the value of ε that will result in equilibrium.

4. I live in the city of Temple Terrace. Our water-treatment plant softens the water using hydrated lime, $Ca(OH)_2$ (*aq*). This chemical can be produced by slaking quicklime, CaO (*s*), according to the following reaction.

$$CaO\ (s)\ +\ H_2O\ (lq)\ \leftrightarrow\ Ca(OH)_2\ (aq)$$

   a. Determine the *standard enthalpy change*, ΔH°, associated with this reaction. Use the standard enthalpies of formation from your text. This value is the heat associated with the reaction *if* all the constituents are present in their standard states. Based on your calculated value of ΔH°, indicate whether heat is released or required as input when quicklime is slaked.

   b. Let's assume that ΔH° is a good approximation to ΔH_{rxn}, which is the change in enthalpy for the reaction at the actual reaction conditions (rather than assuming standard state). I think this assumption is probably pretty good. The heat capacity of water is 4.184 J/(g °C). If CaO is added to water at a concentration of 4×10^{-3} mol/L (which is realistic), how much will the water temperature change? Will the water temperature get warmer or colder when CaO is added?

5. *based on a problem I got from Prof Q Zhang*: Manganese, Mn (II), is soluble in water and is present in many ground waters. Its presence in water may cause taste, staining, and accumulation problems. Ozone (O_3) is sometimes added to water to remove Mn(II) according to the following reaction.

$$Mn^{2+}\ +\ O_3\ (aq)\ +\ H_2O\ \leftrightarrow\ MnO_2\ (s)\ +\ 2\ H^+\ +\ O_2\ (aq)$$

   ΔG° for the above reaction is –164.05 kJ/mole.

   The initial concentrations are Mn^{2+} = 2.0 mg/L, O_3 (*aq*) = 0.48 mg/L, O_2 (*aq*) = 6.4 mg/L. Assume the water has enough alkalinity to neutralize H^+ produced from the reaction, so that pH is maintained at 7 as the reaction proceeds.

problem 5 continues →

5. continued

   a. Determine if the reaction will proceed to form MnO_2 under the given initial concentrations of reactants and products. Hint: assume that activity can be approximated by molar concentration. – except this is not true for H_2O or for MnO_2 (*s*) – for these species, the activity is 1.

   b. Derive the expression of the free energy of the reaction, ΔG, as a function of the extent of reaction, ε.

   c. Determine if the removal of Mn^{2+} can reach 99%. If not, why? What is the maximum conversion?

6. a. Answer question 5-2 in your text. I feel like the text doesn't give enough information to answer this question. Here is what I recommend. Assume that the major cation in the solution is H^+ and that the major anion in the solution is HS^-. If this is true, then we will have the condition that $[H^+] = [HS^-]$. Then if you look up the pK_A for the dissociation of HS^-, you can easily estimate the concentration of S^{2-}. This is probably not the way the book intended us to solve it, but I don't really know what they were thinking. Be sure to tell me where you found the pK_A for HS^-.

   b. Answer question 5-3 in your text, based on your answer to part (a). You will need to look up a constant (which is given in a table in Chapter 5 if you look hard enough). Note: it is possible that you will find *no* more Fe(II) can dissolve – this depends on your answer to part (a). If that is what you determine, the instead calculate the equilibrium concentration of Fe(II) in units of mg/L, after FeS precipitates.

7. Consider the precipitation and dissolution of calcium carbonate, $CaCO_3$.

$$CaCO_3\,(s) \leftrightarrows Ca^{2+} + CO_3^{2-}$$

   a. Calculate $\Delta G°$ and $\Delta H°$ for this reaction at 25 C.

   b. Estimate/calculate the solubility-product constant, K_{SP}, for $CaCO_3$ at 25 C.

   c. Suppose the tap water at your house contains 1×10^{-3} mol/L of Ca^{2+} and 3×10^{-6} mol/L of CO_3^{2-}. These are pretty realistic values, especially if your water supply comes from groundwater and is "hard" – either because you have a private well, or because your city's water supply is from groundwater. Will $CaCO_3$ precipitate spontaneously in your tap water?

   d. Re-calculate the solubility-product constant, K_{SP}, for a temperature of 45 C. Use the formula for temperature dependence of K based on $\Delta H°$.

   e. Referring to parts (a)–(d), explain why your glassware gets spots on it when you wash your dishes in the dishwasher.