ENV 4001: Environmental Systems Engineering

Fall 2021
Problem Set #1
Finish by Wed., Sept. 8, 2021

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This problem set will not be collected or graded. Your reward for completing this problem set is that it is essential for learning the course material and passing the quizzes and final exam.

(1)

(a) Answer problem 3-11 in your text book. Hint #1: the total mass of TCE in the vial after the system equilibrates is equal to the total mass of TCE in the system when it is first introduced. Hint #2: the mass of TCE in the water is equal to the volume of the water times the concentration of TCE in the water.

(b) Answer problem 3-20 in your text book. Hint: notice that the requirement is 1 mg/L of P, not 1 mg/L of PO_4^{3-}. What would be the corresponding concentration of PO_4^{3-}? (...how many moles of P are in 1 mole of PO_4^{3-}? See also p. 51 in the text.)

(2) This problem is based on problems taken from the book *Principles of Environmental Engineering and Science* by Davis and Masten.

For this problem you may assume a temperature of 25 °C.

(a) A water contains 40 mg/L of Mg^{2+}. We want to reduce the concentration of Mg^{2+} in the water, so we raise the pH to 11. What will be the concentration of magnesium ion at that point? Report your answer in units of mg/L. You may assume that the magnesium precipitates as $Mg(OH)_2$.

(b) Groundwater at a particular location contains iron, Fe^{3+}, at a concentration of 1.80 mg/L. We want to raise the pH in order to precipitate out some of the iron as $Fe(OH)_3$. What pH is required to reduce the iron concentration to 0.30 mg/L?

(3) Many years, we don't get to this problem. OK TO SKIP THIS ONE IN 2021.

(a) Balance the following oxidation/reduction (redox) reaction.

$$CH_3CH_2COO^- + a\ SO4^{2-} + b\ OH^- \rightarrow c\ HCO_3^- + d\ HS^- + e\ H_2O$$

(b) What concentration of propionate ($CH_3CH_2COO^-$) would be required to react with 250 mg/L of sulfate? Report your answer in mg/L.

(4) Our air contains carbon dioxide (CO_2) at a concentration of approximately 410–420 parts per million by volume (ppm_v). (This concentration has been rising over the past 60 years – it was 375 ppm the first time I wrote this problem – now it is much higher!) Let's call it 415 ppm for now. (That might be a little optimistic, but OK.)

(a) What is the partial pressure of CO_2 in the air? Report your answer in units of atm, Pa, and torr.

(b) Convert the concentration to units of mg/m^3, assuming an air temperature of 20 °C. Hint: use the ideal gas law along with the partial pressure you found in part (a).

(c) This concentration of CO_2 in the atmosphere has an effect on the pH of rain drops that form in the atmosphere. Consider the following chemical reactions:

$$CO_2\ (g) + H_2O \ <==>\ H_2CO_3\ (aq) \qquad K_H = 3.91 \times 10^{-2}\ \text{M/atm} \qquad \text{[Note the units!!]}$$

$$H_2CO_3 \ <==>\ H^+ + HCO_3^- \qquad pK_A = 6.35\ \text{[so what is } K_A\text{?]}$$

Based on these reactions, and given the CO_2 concentration of 415 ppm_v, determine the pH of rain water that is in equilibrium with the air. Is rain water acidic or basic? Hint: you have three unknowns: $[H_2CO_3]$, $[H^+]$, and $[HCO_3^-]$. You are given two equilibrium equations. Therefore you need one more equation to solve the problem. The third equation is based on electroneutrality, and the important result is that $[H^+] = [HCO_3^-]$. With this third equation, you should be able to solve the problem. Note that you won't always have $[H^+] = [HCO_3^-]$, so don't assume that is a general rule, but it works in this particular case (for reasons we won't go into here).

(5) One of Prof Cunningham's former students wrote his doctoral dissertation about a new technology to clean up soil contaminated by certain types of chemicals. One of the chemicals we tested in the lab was 1,2,4,5-tetrachlorobenzene (TeCB).

(a) Draw the chemical structure of 1,2,4,5-tetrachlorobenzene.

(b) When we started working on the project, we thought maybe TeCB would be destroyed according to first-order kinetics, but we weren't sure. Below are two tables of actual data that the student collected in the laboratory. The two data sets were collected under different experimental conditions. For each of the two experiments, determine if the disappearance of TeCB is zero-order, first-order, second-order, or something else. Specify the value of the rate constant (k_0, k_1, or k_2, as appropriate). Be sure to give the right units of k!

Table 1: Concentration of TeCB vs. time, experiment 1

time (min)	Conc. (mg/L)
0	5.0
5	2.93
10	2.06
20	0.61
30	0.28
45	0.057

Table 2: Concentration of TeCB vs. time, experiment 2

time (min)	Conc. (mg/L)
10	3.02
20	2.51
30	2.16
45	1.59
60	1.07

If you want to know more about this project, read the following papers:

Wee HY, Cunningham JA, 2008. Palladium-catalyzed hydrodehalogenation of 1,2,4,5-tetrachlorobenzene in water-ethanol mixtures. *Journal of Hazardous Materials*, vol. 155, pp. 1–9.

Wee HY, Cunningham JA, 2011. Remediation of contaminated soil by solvent extraction and catalytic hydrodehalogenation: Semicontinuous process with solvent recycle. *Environmental Progress & Sustainable Energy*, vol. 30, no. 4, pp. 589–598.

(6) *Note:Many years, I don't get to spend a lot of class time teaching about alkalinity and buffer capacity, so you might have to do some reading in the text book to figure out the details of this problem. Or ask me for some help in office hours.*

Suppose a particular water sample is known to have pH = 8.34 and $[HCO_3^-]$ = 183 mg/L.

(a) Estimate or calculate the *molar* concentrations of HCO_3^-, H^+, OH^-, H_2CO_3, and CO_3^{2-}. Hint: yes, you have enough information to do these calculations.

(b) Suppose that the only other ion present in the water is sodium, Na^+. Estimate or calculate the molar concentration of Na^+ that would be required to ensure charge neutrality in the water: $[Na^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$.

(c) Estimate or calculate the *alkalinity* of the water sample. Report the alkalinity as normality (eq/L) and as mg/L of $CaCO_3$. You can look up an equation for alkalinity in the text book if we don't get to it in class. Also see p. 52 in the text.

(d) Repeat parts (a)–(c) if the pH is 8.34 (as it was before), but now the concentration of bicarbonate is $[HCO_3^-]$ = 30 mg/L.

(e) Now suppose you have two beakers. In the first beaker, you put 99 mL of the first water sample (183 mg/L bicarbonate) and you add 1 mL of hydrochloric acid (HCl). The concentration of the HCl (before addition to the water sample) is 0.1 M, which is also equal to 0.1 N. In the second beaker, you put 99 mL of the second water sample (30 mg/L bicarbonate) and you add 1 mL of HCl. You allow both mixtures to equilibrate, and then you measure the pH in both beakers. What do you think you will see? Why? Hint: it is possible to actually calculate the pH in each beaker, but that is a pretty complicated calculation, and it is beyond the scope of ENV 4001; try for a qualitative answer here. Will the pH go up or down in the first beaker? By a little or by a lot? Why? What about in the second beaker? Why?

(7) Look up two of the Sustainable Development Goals that seem like they would be particularly relevant for ENV 4001. Write down the number and the title (e.g., Goal 4, "Quality Education") of these two SDGs. Then, look up the brief description of these two goals and write those down too (e.g., "Ensure inclusive and quality education for all and promote lifelong learning"). Try to memorize the numbers, the names of the goals, and the brief description of the goals.