

ENV 6519: Physical & Chemical Processes for Groundwater Remediation

Spring 2021
Homework #6
Due Tues., Mar. 2, 2021

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1. (35 pts) Refer to the following two papers.

Gossett JM, 1987. Measurement of Henry's Law constants for C1 and C2 chlorinated hydrocarbons. *Environmental Science & Technology*, 21(2), 202–208.

Ashworth RA, Howe GB, Mullins ME, Rogers TN, 1988. Air-water partitioning coefficients of organics in dilute aqueous solutions. *Journal of Hazardous Materials*, 18(1), 25–36.

- (a) From these two papers, compile a table of measured Henry's constants for the following four compounds: tetrachloroethylene (also called perchloroethylene, or PCE), trichloroethylene (TCE), carbon tetrachloride (CT), and chloroform (CF). Put the data from both papers into a single table. Your table should cover measured values from 9.6 °C to 34.6 °C. Express H in dimensionless form, i.e., $H = C_i^{\text{air}}/C_i^{\text{water}}$. This might require you to manipulate the data from the papers somewhat to get the units right.
- (b) For each chemical, prepare a graph showing the temperature dependence of H. Prepare your graph by plotting $\ln(H)$ vs $1/T$ over the applicable temperature range. (What units for T?) For each chemical, make just one graph that uses the data from both papers (i.e., do not make two separate graphs for each chemical). Do the data appear to lie on straight lines when graphed in this manner?
- (c) How well do the two papers seem to agree? Do there appear to be any significant discrepancies between the values reported in the two papers?
- (d) From your graphs in part (b), estimate the heat of vaporization for each of the four chemicals. Report your answers in units of kJ/mol and kcal/mol.
- (e) Look up the heats of vaporization in a reliable source. (For instance, I have the 65th edition of the *CRC Handbook of Chemistry and Physics*, and the heats of vaporization are given on page C694. You can use whatever authoritative source you like, but *please give the complete citation for that source.*) Compare your calculated values to those that you looked up. How closely do your estimates agree with the tabulated values?
- (f) Look up the vapor pressure and the aqueous solubility of these four compounds at 25 °C. You can find these in the appendix of *Environmental Organic Chemistry* [Schwarzenbach RP, Gschwend PM, and Imboden DM, 2nd edition, 2003], or perhaps from a *reliable* source on the Internet. Use the vapor pressure and the aqueous solubility to predict H for the four compounds at that temperature. How do your predicted values of H compare to the experimental values of Ashworth and Gossett at that temperature? Do you find this estimation method to be trustworthy? Would you trust this method if you needed to estimate H, say, for the purposes of designing an air stripping tower?

2. (30 pts) Suppose you have a contaminated water stream that flows at $Q = 100$ L/min and contains TCE at a concentration of $C_0 = 1000$ $\mu\text{g/L}$. The temperature is 22 $^\circ\text{C}$, and you may assume Henry's constant for TCE is $H = 0.40$ at that temperature. You want to use air stripping to treat the water down to a concentration of $C_e = 100$ $\mu\text{g/L}$. The air flow rate is $Q_a = 750$ L/min, and the air is initially clean (i.e., the influent air contains no TCE).

- What is the stripping factor?
- Suppose that, at this air flow rate, you are able to achieve your treatment objective, and the concentration of TCE in the effluent water is exactly $C_e = 100$ $\mu\text{g/L}$. What will be the concentration of TCE in the air leaving the top of the tower? Hint: use a mass balance!
- Find the concentration difference $\Delta C_{\text{top}} = C - C^*$ at the top of the tower. In other words, find the difference between the actual aqueous concentration (known to be 1000 $\mu\text{g/L}$) and the *hypothetical aqueous concentration*, C^* , that would be in equilibrium with the exiting air. Hint: To find C^* , use your answer to part (b) along with Henry's law.
- Find the concentration difference $\Delta C_{\text{bottom}} = C - C^*$ at the bottom of the column. Hint: what is C at the bottom of the tower? Another hint: at the bottom of the tower, C^* means the hypothetical aqueous concentration that would be in equilibrium with the *entering* air; no calculations are necessary to determine C^* at the bottom of the tower.
- Find the *log-mean average concentration difference* in the tower. This is a way of averaging ΔC_{top} with ΔC_{bottom} . Here is the formula for calculating that:

$$\overline{\Delta C} = \frac{\Delta C_1 - \Delta C_2}{\ln(\Delta C_1 / \Delta C_2)}$$

- Estimate the number of transfer units (NTU) according to the following formula:

$$NTU = \int_{C_e}^{C_0} \frac{dC}{C - C^*} \approx \frac{C_0 - C_e}{\overline{\Delta C}}$$

This is a way chemical engineers sometimes estimate NTU. They use the log-mean average concentration difference (or, in heat transfer applications, the log-mean average temperature difference) based on the known conditions at the top and the bottom of the tower.

- Now estimate NTU according to equation 14-50 in your text. How does this estimate compare to the number you calculated in part (f)? Do the chemical engineers appear to know what they are doing?
- Now construct the McCabe-Thiele diagram for this problem. Use the diagram to estimate the number of equilibrium stages (also called number of theoretical plates, or NTP) in a staged cascade that would be required to meet the treatment objective. How does your estimate of NTP compare to your two estimates of NTU, above?

3. (15 pts) Repeat problem 2, parts (a)–(h), if the air flow rate is 250 L/min instead of 750 L/min. You will run into a couple snags with the math. For part (e), instead of using the formula given, think about what the *average* concentration difference ought to be for the new air flow rate. For part (g), you will have trouble applying equation 14-50. However, if you love math, you can use L'Hopital's rule on 14-50 to derive an appropriate formula for NTU. (It turns out that L'Hopital's rule is actually useful...who knew?) I tried this and I got

$$\lim_{S \rightarrow 1} NTU = \frac{C_0}{C_e} - 1$$

which you can use if you trust my mathematical capabilities. If you are skeptical about my math ability, then you will have to come up a different way to calculate NTU for part (g).

[Aside: If we need, say, 99% removal of a chemical, then $C_0/C_e = 100$, and we'd get 99 NTU at a stripping factor $S = 1$. That would be a tall tower!! – so this shows us that if we need a high removal fraction, we had better use a higher air flow rate. Using $S = 1$ won't work well.]

4. (5 pts) I read in a chemical engineering text book [McCabe WL, Smith JC, Harriott P, 1985; Unit Operations of Chemical Engineering, 4th edition; McGraw-Hill, New York, NY; pp 629–630] that “the number of transfer units is somewhat like the number of theoretical stages, but these values are equal only if the operating line and the equilibrium line are straight and parallel.” Are your findings from problems (2) and (3) consistent with this statement? Explain briefly (a couple sentences should probably suffice). (You can also read the top of p 1073 in your text book for more about the equivalence of NTU and NTP.)
5. (15 pts) Starting with equation 14-42 in your text, derive equation 14-47. The text provides some of the derivation for you in equations 14-43 through 14-46. Complete the derivation by filling in all the algebraic steps left out by the text. It probably ought to take you a page or two (depending on how small you write).
6. BONUS – NOT GRADED – JUST FOR FUN.
Complete problem 14-6 in your text book.

7. BONUS -- NOT GRADED -- JUST FOR FUN.

Look at the data in Tables I, II, and IV of the following paper:

Leighton DT Jr., Calo JM, 1981. Distribution coefficients of chlorinated hydrocarbons in dilute air-water systems for groundwater contamination. *Journal of Chemical and Engineering Data*, 26(4), 382–385.

These tables have data for the same four chemicals that you considered above in problem 1. Prepare graphs of $\ln(H)$ vs $1/T$ for the data of Leighton & Calo. You can compute H by taking the “distribution coefficient” and dividing by 1000. How do the graphs of the Leighton & Calo data compare to the graphs you prepared above?