ENV 6519: Physical & Chemical Processes for Groundwater Remediation

Spring 2019   University of South Florida
Homework #2   Civil & Environmental Eng.
Due Thurs., Jan. 28, 2021   J. A. Cunningham

(1) (25 pts)

This semester, we will learn to clean up water that is contaminated with a hazardous chemical. In class, I gave you a formula for how much energy is required to recover a pure liquid chemical out of an aqueous solution in which the chemical's concentration is C. Now let's use the formula to perform some useful calculations.

(a) (5 pts) Assume that you have a volume V of water, and it contains a concentration C of some contaminant (where C has units of mass per volume). You perform a separation and you remove a very small amount of the contaminant from the water. The change in the contaminant concentration is ΔC, and the mass of contaminant that you removed is $V \Delta C$. How much energy is required to remove the small amount of mass? For this, you may assume that $\Delta C \ll C$. Hint #1: you have a formula that tells you how much energy is required per mole of contaminant recovered. Hint #2: this problem is really simple; don't try to make it complicated. It should only take a line or two and does not require any complicated derivations.

(b) (5 pts) Now suppose I have a volume V of water that initially contains a concentration C_0 of the contaminant. I want to treat the water and reduce the contaminant concentration down to C_f. Argue that the energy required for this treatment is given by this formula:

$$V \frac{RT}{MW} \int_{C_f}^{C_0} \ln\left(\frac{C^{SL}}{C}\right) dC$$

where MW is the molecular weight of the contaminant, and C^{SL} is the solubility-limit concentration, in units of mass per volume.

(c) (10 pts) Now we are ready to perform an actual calculation. Suppose I have water contaminated with tetrachloroethene (also called tetrachloroethylene, perchloroethene, perchloroethylene, PCE, or PERC) at a concentration of 5 mg/L. I want to treat this water to get the PERC concentration down to 5 μg/L, which is the federal drinking-water standard. What is the minimum energy requirement to treat 1000 L of contaminated water? Hint #1: use the formula from part (c), and use an integral table if you are rusty on your integration. Hint #2, to help you with the integration: how is $\ln(a/x)$ related to $\ln(x/a)$? Which is easier to integrate? Hint #3: you will have to look up the aqueous solubility of PERC; I do not think the Wikipedia entry for tetrachloroethylene is correct; try to find a better source.

(d) (5 pts) In part (c) you found the energy required. How many moles of PERC did you recover? How much energy did you expend per mole? (Report this answer in units of kJ/mol.)

(2) (10 pts)

  (a) (7 pts) Complete problem 7-11 in the Water Treatment text book.

  (b) (3 pts) Compare the magnitude of the oxygen mass-transfer coefficient to the PCE mass-transfer coefficient. Which is higher? By how much? Why?

(3) (25 pts)

  (a) (6 pts) Use the Hayduk-Laudie method to estimate the aqueous diffusion coefficients for ethanol at 25^OC, ethylbenzene at 20^OC, phenol at 20^OC, and vinyl chloride at 25^OC. Use the method of LeBas to calculate the molar volumes V_b. Don't forget the "ring reductions" when calculating V_b. You will have to look up the viscosity of water at the two different temperatures; I think your text book has an appendix with that information.

  (b) (6 pts) Re-do the calculation from part (a), but calculate the molar volume as the molecular weight divided by the liquid density: $V_b = MW/\rho$. Molecular weights should be easy enough to calculate if you know the structures of these chemicals. Liquid densities might be more difficult to find. Two possible sources are the CRC Handbook or Wikipedia. I do not know how reliable Wikipedia is – probably pretty good, but I am not positive.

  (c) (4 pts) Compare the values you got in parts (a) and (b) to the values listed in Table 7-1. Which method of estimating V_b gives a closer match to the experimentally measured values? For whichever method you think is better, estimate/calculate the relative error between the measured value and the predicted value. Assume that the measured value is the "correct" value.

  (d) (3 pts) Based on your results, how much uncertainty do you think there is in this estimation method? Do you trust your estimated values to $\pm 1\%$? to $\pm 10\%$? to within a factor of two? Based on this, how many significant digits do you think are warranted when you report a diffusion coefficient estimated with the Hayduk-Laudie method?

  (c) (6 pts) The chemicals in your design project this semester are trichloroethene (TCE), cis-1,2-dichloroethene (DCE), and 1,1,2,2-tetrachloroethane (TeCA). Values for the aqueous diffusion coefficient are not listed in Table 7-1 for these chemicals. Use the Hayduk-Laudie method to estimate the aqueous diffusion coefficients for TCE, DCE, and 1,1,2,2-TeCA at a temperature of 18 ^{O}C.

(4) (20 pts)

  (a) (10 pts) Complete problem 7-12 in the Water Treatment text book. Hint: for each of the five bottles, you can calculate the adsorbed concentration q using methods given in the text book. Then, prepare a figure like Figure 7-7 in your text. Don't forget to specify the V/M ratios. The phase equilibrium line – that is, the graph of q versus C – is also called a *sorption isotherm*.

  (b) (10 pts) Graph q vs C on a log-log scale, i.e., graph $\log(q)$ vs. $\log(C)$. If $\log(q)$ is linear with respect to $\log(C)$, then the data are said to obey a *Freundlich isotherm*. Fit a straight line through the graph on the log-log plot. (You can do this in Excel, but it requires a little thought – if you do it wrong, you won't get a straight line on your log-log plot.) How good is the straight-line fit? Do you think a Freundlich isotherm applies to these data?

(5) (20 pts)

   (a) (8 pts) Using the method described in your text book, estimate the diffusion coefficient for tetra-chloroethene (also called tetrachloroethylene, perchloroethene, perchloroethylene, PCE, or PERC) in air at 20 $^{\text{o}}$C.

   (b) (8 pts) Repeat the calculation using the method of Arnold [Arnold, J.H., 1930; "Studies in Diffusion, I – Estimation of Diffusivities in Gaseous Systems." *Industrial and Engineering Chemistry*, vol. 22, no. 10, pp. 1091–1095]:

$$D_{12} = \frac{0.00837 \, T^{5/2} \, [(M_1 + M_2)/M_1 M_2]^{0.5}}{P \left(V_{b1}^{1/3} + V_{b2}^{1/3} \right)^2 (T + S_{12})}$$

where D_{12} is the diffusion coefficient of gas 1 in gas 2, in units of cm^2/s; T is the temperature in degrees Kelvin; M_1 and M_2 are the molecular weights (in g/mole) of compounds 1 and 2; P is the pressure in atmospheres; V_{b1} and V_{b2} are the molar volumes (in cm^3/mole) of the gases at their normal boiling points; and S_{12} is given by the following.

$$S_{12} = 1.47 \, F \, \sqrt{T_{b1} \, T_{b2}}$$

$$F = \left[\frac{2 \sqrt{V_{b1} \, V_{b2}}}{V_{b1} + V_{b2}} \right]^{(1/3)}$$

where T_{b1} and T_{b2} are the normal boiling points of the two gases, in degrees Kelvin.

For this problem, you can assume that the boiling point of air is 79 K, and the air is at 1 atmosphere. You can calculate the molecular weight of air based on knowing its composition, and you can look up its molar volume in Table 7-3 of your text. Also, you can estimate the molar volume of PCE using techniques given in the text, and you can look up the boiling point of PCE (it would be good to cite your source).

   (c) (4 pts) How well do the two methods agree? Which did you find easier? Based on the level of agreement, how many significant digits do you think are warranted in your estimates?

(6) OPTIONAL QUESTION – NO POINTS ASSIGNED.

Based on your estimates in problems (3) and (5), what is the relative magnitude of the diffusion coefficient in air to the diffusion coefficient in water? i.e., what is (approximately) the ratio of D from problem (5) to those of problem (3)? (Although you considered different chemicals in problems 3 and 5, they are all of similar size and molecular weight, so comparing the values of D for the different chemicals is fine to give us a semi-quantitative estimate, which is all we want here.) Based on this, would you expect gas-phase mass transfer coefficients to be larger or smaller than liquid-phase mass transfer coefficients? By a little or by a lot?