

ENV 6002: Physical and Chemical Principles of Environmental Engineering

Fall 2008

Homework #6

Due: Tues., Oct. 21...but get it done by 10/16

University of South Florida

Civil & Environmental Eng.

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1. (25 pts)

- a. Using the O'Connor-Dobbins relationship, estimate the individual mass transfer coefficient, k_L , for reaeration (i.e., the transfer of molecular oxygen, O_2) in a river having an average depth of 1.0 m and an average velocity of 0.20 m/sec, at $T = 20^\circ\text{C}$. Assume that the molecular diffusivity of O_2 in water is $2.1 \times 10^{-9} \text{ m}^2/\text{sec}$ at that temperature.
- b. Assume that the liquid-phase resistance controls the overall mass transfer rate. Use this assumption to estimate the overall mass transfer coefficient, K_L , in units of m/sec. Also estimate the mass transfer rate constant, $K_L a$, in units of 1/sec.
- c. Now let's see if the assumption made in part (b) is valid. Calculate a revised estimate for the overall mass transfer rate constant, $K_L a$, for oxygen under the conditions of part (a), but this time accounting for the gas-phase resistance. Assume that $k_G/k_L = 100$ and $H_{cc} = 30$ for oxygen at 20°C .
- d. Compare your estimate of $K_L a$ from part (b) to your estimate from part (c). What do you conclude about the importance of the gas-phase resistance for oxygen? Can it safely be neglected in engineering calculations?
- e. To conclude the investigation of the importance of gas-phase resistance for oxygen transfer, calculate the fraction of the overall mass transfer resistance that is attributable to the gas phase. Hint: the overall resistance is the sum of the liquid-phase resistance and the gas-phase resistance.
- f. For ethanol, C_2H_5OH , at the same conditions as above, calculate k_L , k_G , K_L , and $K_L a$. Given: $D^L = 1.24 \times 10^{-9} \text{ m}^2/\text{s}$, and $H_{CC} = 2.7 \times 10^{-4}$. Is the assumption of liquid-phase control valid for the transfer of ethanol from the river to the atmosphere?
- g. Compare the values of k_L for O_2 and ethanol: are they about the same, or pretty different? What about the values of K_L ? Explain why you see these patterns.
- h. Ethanol (C_2H_5OH) degrades completely under the conditions in the river, with a decay rate constant of 0.5/day. Considering the results obtained above, which of the two processes governs the rate of ethanol loss from solution: transfer to the atmosphere, or degradation? Justify your answer.

2. (25 pts) Chloroform (also called trichloromethane, CHCl_3) is present in municipal water supplies because it is formed as a disinfection by-product when water is chlorinated. In the city of Temple Terrace, where I live, the concentration of chloroform in the water is about $45 \mu\text{g/L}$. When a person takes a hot shower, some fraction of that chloroform undergoes inter-phase mass transfer from the water phase to the air phase. Breathing the air in the shower is one of the primary routes of exposure to chloroform (which is a known carcinogen).

In this problem, we will estimate how much chloroform volatilizes out of a droplet of water in the shower. Assume that a typical water droplet is approximately spherical with a diameter $d = 2.0 \text{ mm}$. Assume that the shower head is 2.0 m above the floor of the shower, and that the droplet falls through the air with a velocity $u = 1.0 \text{ m/sec}$. All of these are approximations, but they might be pretty close. Assume that the water temperature and the air temperature are both 37 C ; this is probably not valid for the air, but we'll hope that not much error is introduced.

- a. Estimate Henry's constant (H_{cc} form) for chloroform at 37 C . You'll need it for later in this problem.
- b. Estimate the individual mass-transfer coefficients, k_L and k_G , for the inter-phase mass transfer of chloroform out of a falling drop. I found these relationships in a chemical engineering text book*:

$$k_L = 10 D^{aq}/d$$

$$k_G = 2 [(D^{air} u)/(\pi d)]^{0.5}$$

where D^{aq} is the diffusivity of chloroform in water, and D^{air} is the diffusivity of chloroform in air. Next semester in ENV 6519 you will learn how to estimate D^{aq} and D^{air} ; for now, you can use $D^{aq} = 1.3 \times 10^{-9} \text{ m}^2/\text{sec}$ and $D^{air} = 1.2 \times 10^{-5} \text{ m}^2/\text{sec}$ at 37 C .

[*Reference: McCabe, W.L., Smith, J.C., & Harriott, P., 1985. *Unit Operations of Chemical Engineering*, 4th edition. McGraw-Hill, New York.]

- c. Use k_L , k_G , and H_{cc} to estimate K_L , the overall mass-transfer coefficient for chloroform volatilization. Which mass-transfer resistance is dominant, liquid or gas? (Or are both resistances important?)
- d. Estimate a , the specific interfacial area of a falling droplet, and $K_L a$, the mass transfer rate constant.
- e. Write an expression for the flux, J , of chloroform from the droplet to the air. Write J as the product of a mass transfer coefficient and a concentration difference. Define flux as positive from the water to the air.

problem 2 continues →

2. continued

- f. Assume that the concentration of chloroform in the air is pretty low -- low enough that we can consider it to be zero. How does that affect your expression for J in part (e)?
- g. Write a material balance for the mass of chloroform in the water droplet at the droplet falls. Use this material balance to derive a differential equation for the concentration of chloroform in the water droplet.
- h. Solve the differential equation. If the concentration of chloroform in the droplet is 45 mg/L when the droplet exits the shower head, what is the concentration in the droplet when the droplet lands on the floor of the shower? What fraction of the chloroform volatilizes into the air as the droplet falls to the floor?

A note about this problem. I think the biggest source of uncertainty in this problem is the estimates of k_L and k_G . Although chemical engineers have spent a lot of time thinking about mass transfer in falling droplets, it is difficult to characterize the fluid mechanics of a droplet as it falls -- how much internal circulation is there? This can strongly affect the estimate of k_L . The droplet size is also important, so if my estimate of d is poor, that could create some error in the solution, but I think the estimate of k_L is probably where most of the uncertainty arises. I don't know what the "right" answer is! -- but it is fun to try it this way, isn't it?

NOT REQUIRED FOR FALL 2008:

3. (0 pts) Consider the mass transfer of 2,2',5,5'-tetrachlorobiphenyl (a PCB) from river water to air. The temperature is 25 °C, and the river has an average velocity $u = 0.40$ m/sec and a depth $H = 0.50$ m. You may assume that $k_G/k_L = 100$ under these conditions. The aqueous diffusivity of the PCB is 0.80×10^{-9} m²/s. Other data for 2,2',5,5'-tetrachlorobiphenyl can be looked up in Section 4B of your reader.
 - a. Calculate the overall mass transfer coefficient, K_L , and the rate constant, $K_L a$, for transfer of 2,2',5,5'-tetrachlorobiphenyl from the river water to the air.
 - b. Is an assumption of liquid-phase control of the mass transfer rate justified? Explain.