

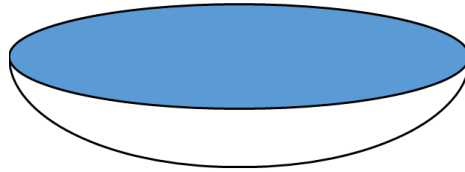
## Fate & Transport of Chemicals in the Environment

Homework #5  
Due Monday, Feb. 21, 2022

University of South Florida  
Prof J A Cunningham

1. (20 pts) *Based on a problem originally written by Prof Paul Roberts of Stanford University*
  - 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/s, at  $T = 20\text{ }^\circ\text{C}$ . Assume that the molecular diffusivity of  $O_2$  in water is  $2.1 \times 10^{-9}\text{ m}^2/\text{s}$  at that temperature. Report your estimate of  $k_l$  in units m/s.
  - b. Assume for now that the liquid-phase resistance controls the overall mass transfer rate. Use this assumption to estimate the overall mass transfer coefficient,  $k_{LO}$ , in units m/s.
  - c. Now let's see if the assumption made in part (b) is valid. Calculate a revised estimate for the overall mass transfer coefficient,  $k_{LO}$ , for oxygen under the conditions of part (a), but this time accounting for the gas-phase resistance. Assume that  $k_g/k_l = 50$  and  $H_{cc} = 30$  for oxygen at  $20\text{ }^\circ\text{C}$ .
  - d. Compare your estimate of  $k_{LO}$  from part (c) to your estimate from part (b). 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 (or percentage) 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  $k_l$ ,  $k_g$ , and  $k_{LO}$ . Given:  $D^{aq} = 1.24 \times 10^{-9}\text{ m}^2/\text{s}$ ,  $H_{CC} = 2.7 \times 10^{-4}$ , and  $k_g/k_l = 50$  as before. 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  $k_{LO}$ ? – about the same, or pretty different? Explain why you see these patterns.

2. WE WILL DO THIS ONE AS AN EXAMPLE IN CLASS. Alpine Lake is a popular place for fishing. Alpine Lake is shaped like the bottom half of an ellipsoid:



In a year with average rainfall, the lake is 1000 m across the middle in the “long” direction, 500 m across the middle in the “short” direction, and 20 m deep at its deepest point.

When the oxygen concentration in the lake water decreases below 7.7 mg/L, the population of Alpine Trout decreases sharply, and the Game Warden won’t let anybody fish. Some avid fishermen (fisherpeople?) have hired you to help them by answering the following questions.

- What is the concentration of oxygen in the air, expressed as mg/L, at 20 °C? Hint: air is 21% oxygen by moles or by volume.
- What is  $C^*$ , the aqueous concentration (expressed in mg/L) that would hypothetically be in equilibrium with the atmosphere? Assume the air and the water are both at 20 °C. The dimensionless Henry’s constant for oxygen at 20 °C is  $H_{CC} = 30$ .
- You measure the oxygen concentration in the lake and find that it is 5.0 mg/L. Based on this information, is the system at equilibrium? If not, which way is the oxygen moving? (i.e., from the air to the water, or from the water to the air?)
- Write an equation for the flux of oxygen across the surface of the lake, in terms of a mass transfer coefficient and a concentration difference. Define flux into the lake to be positive. Your equation should include the overall mass-transfer coefficient  $k_{LO}$ .
- Perform a mass balance for the mass of oxygen in Alpine Lake to get the following equation:

$$\frac{d}{dt} [\text{mass of oxygen in lake}] = A J$$

where  $A$  is the surface area of the lake and  $J$  is the flux of oxygen into the lake.

(Note: This equation only works if the lake water is well-mixed. Not all lakes are well-mixed, but Alpine Lake is not very deep, so an assumption of well-mixed is probably OK. Therefore we think this equation should be fine for Alpine Lake.)

- Take the equation above, but re-write “mass of oxygen in the lake” in terms of the *concentration* of oxygen in the lake. Also express the flux,  $J$ , in terms of the concentration of oxygen in the lake. What differential equation do you get?

problem 2 continues →

2. continued

- g. If you haven't done so already, re-arrange the differential equation from part (e) until it is in the form  $dC/dt = \dots$ , where  $C$  is the concentration of oxygen in the lake.
- h. The ratio  $A/V$  (where  $V$  is the volume of the system of interest – in this case, the volume of the lake) is called the “specific interfacial area.” Specific interfacial area is usually denoted by the symbol  $a$ , i.e.,  $a = A/V$ . Using the geometry of an ellipsoid, determine the specific interfacial area of Alpine Lake. Be sure to specify the units on  $a$ .

Hint 1: the area of an ellipse is  $\pi b c$  if  $b$  and  $c$  are the semi-major axis lengths.

Hint 2: the volume of an ellipsoid is  $(4/3)\pi b c d$  if  $b$ ,  $c$ , and  $d$  are the semi-major axis lengths (with  $d$  being the depth of the lake in this case).

Hint 3: Alpine Lake is only the bottom half of an ellipsoid.

- i. Solve the differential equation from part (f). Your answer should be in the form  $C(t) = \dots$
- j. If we know that the overall mass transfer coefficient for re-aeration,  $k_{LO}$ , has a value of 0.4 m/d, determine how long we must wait before we can fish in the lake again.

3. (40 pts) Chloroform (also called trichloromethane,  $\text{CHCl}_3$ ) 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  $2.0 \text{ m}$  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 is  $37 \text{ }^\circ\text{C}$ .

- a. Estimate the individual mass-transfer coefficient,  $k_l$ , for the inter-phase mass transfer of chloroform out of a falling drop. Through the years, many correlations have been suggested for mass transfer to/from falling drops. For this assignment, we will use the following\*:

$$\frac{k_l d}{D^{aq}} = 2.0 + 0.6 \left( \frac{\rho_L u d}{\mu_L} \right)^{1/2} \left( \frac{\mu_L}{\rho_L D^{aq}} \right)^{1/3}$$

where  $D^{aq}$  is the diffusivity of chloroform in water,  $\rho_L$  is the density of the water, and  $\mu_L$  is the viscosity of the water. You can use  $D^{aq} = 1.3 \times 10^{-9} \text{ m}^2/\text{s}$  at  $37 \text{ }^\circ\text{C}$ .

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

- b. Estimate Henry's constant ( $H_{CC}$  form) for chloroform at  $25 \text{ }^\circ\text{C}$ . We know the value of  $H_{CC}$  at  $37 \text{ }^\circ\text{C}$  will be even higher than the value at  $25 \text{ }^\circ\text{C}$ .
- c. Let's assume  $k_g/k_l = 75$  for our droplet. Using this assumption, along with your answer from part (b), argue that it is acceptable to ignore gas-side resistance to mass transfer from the droplet. What does this mean for  $k_{LO}$ ?
- d. Estimate  $a$ , the specific interfacial area of a falling droplet, and  $k_{LO} a$ , the mass transfer rate constant. Recall that specific interfacial area is the ratio  $A/V$ , where  $A$  is the air-water interfacial area, and  $V$  is the volume of the droplet.
- 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.
- 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)?

problem 3 continues →

3. continued

- g. Perform a mass balance for the mass of chloroform in the falling droplet, to get the following equation:

$$\frac{d}{dt}[\text{mass of chloroform in droplet}] = -A J$$

where  $A$  is the surface area of the droplet and  $J$  is the flux of chloroform from the droplet to the air.

- h. Why is it  $-A J$  on the right-hand side in this problem, but it was  $+A J$  on the right-hand side in problem 2?
- i. Use the mass balance above, but re-write “mass of chloroform in droplet” in terms of the *concentration* of the chloroform in the droplet. Also re-write the flux,  $J$ , in terms of concentration. Derive a differential equation for the concentration of chloroform in the water droplet. It should be in the form  $dC/dt = \dots$
- j. Solve the differential equation. If the concentration of chloroform in the droplet is  $45 \mu\text{g/L}$  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?
- k. BONUS -- NOT REQUIRED. Estimate the mass of chloroform that a person inhales during a 15-minute shower. Assume the flow rate of the water is  $8 \text{ L/min}$ . Assume that the person in the shower inhales half of the chloroform that is released from the droplets. Compare the mass of chloroform inhaled to the mass that would be ingested by drinking  $2 \text{ L/d}$  of tap water. Which gives a higher dose, showering or drinking?

A note: I think the biggest source of uncertainty in this problem is the estimate of  $k_1$ . 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  $k_1$ . 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  $k_1$  is probably where most of the uncertainty arises. I don't know what the “right” answer is! – we make our best estimates. It is a fun problem anyway!

4. (40 pts) Suppose we have a beaker of water with a large globule of trichloroethene (TCE) at the bottom of the beaker. We are trying to get the TCE to dissolve into the water, so we stir the water with a mechanical impeller. The power provided to the mechanical impeller,  $P$ , is 30 W (the same power as a dim light bulb). The volume of water in the beaker,  $V$ , is 500 mL. The diameter of the TCE globule,  $d$ , is 5.0 cm.
- Why does the globule of TCE reside on the bottom of the beaker instead of floating in the water or floating on the top of the water?
  - If we stir the beaker long enough, eventually the system will reach equilibrium. When that happens, what will be the concentration of TCE in the water? Report your answer in units of mg/L. Hint: use a table in your text book.

When we first set up the system, the water is clean, i.e., it does not contain any TCE in it. Let's find out how long it takes for the TCE concentration in the water to reach a value of 300 mg/L.

- Write a mass balance for the mass of TCE in the water. In your mass balance, include the flux of TCE from the NAPL phase into the aqueous phase. Use the symbol  $J$  to represent flux. Other terms in your mass balance should be the volume of water ( $V$ ), the concentration of TCE in the water ( $C$ ), and the interfacial area ( $A$ ) between the TCE and the water. Your answer to this part of the problem should be a differential equation.
- Assume that the globule of TCE is a hemisphere with a diameter  $d = 5.0$  cm. What is the interfacial area,  $A$ , between the TCE globule and the water? What is the specific interfacial area,  $a = A/V$ ? – report your value of  $a$  in units of  $\text{m}^{-1}$ .
- Now re-write the mass balance, but this time, re-write the flux term,  $J$ , in terms of a mass-transfer coefficient,  $k_{LO}$ , and a concentration difference. Write the concentration difference in a manner so that the flux,  $J$ , is positive. This part of the problem is pretty easy except for figuring out what concentration difference to use. Hint: what was your answer to part (b)? Another hint: when the system is at equilibrium, what should be the value of  $J$ ?
- Now you should have a differential equation that you can solve! Solve the differential equation to derive an equation  $C(t) = \dots$ . Your answer will be written in terms of  $a$ ,  $k_{LO}$ ,  $t$ , and maybe one or two other things also. Hint: to solve the differential equation, you need to use an initial condition. Remember that the water is clean at time  $t = 0$ .
- You have values for most of the things in your equation, but we need a value of  $k_{LO}$ . We can neglect mass-transfer resistance on the TCE side of the globule, so  $k_{LO} \approx k_l$ . I found this equation for  $k_l$  for a stirred beaker:

$$k_l = 0.13 \left( \frac{D^{\text{aq}}}{\nu} \right)^{2/3} \left( \frac{P \nu}{\rho V} \right)^{1/4}$$

where  $\rho$  and  $\nu$  are the density and (kinematic) viscosity of the water, respectively. Assume 25 °C. Also, for TCE in water at 25 °C,  $D^{\text{aq}} \approx 0.85 \times 10^{-9} \text{ m}^2/\text{s}$ .

Estimate/calculate the value of  $k_{LO}$ . Report your answer in m/s. Watch your units!

- How long until the TCE concentration in the water reaches a value of 300 mg/L?

5. (40 pts) Suppose you have a groundwater site contaminated by trichloroethylene (TCE) and by 1,4-dioxane. This is a very common situation: these contaminants are frequently found together because 1,4-dioxane is used as an additive to TCE-based solvents. We are planning to treat the groundwater with an air stripping tower – this is a very common treatment technique. An air stripping tower works by moving the contaminants from the water phase to the air phase. (This cleans up the water, but it makes the air dirty. Sometimes that is OK. We will assume it is OK here.)

In the process of designing the air stripping tower, one of the important steps is to estimate the mass-transfer coefficients  $k_l$ ,  $k_g$ , and  $k_{LO}$  for the transfer of the contaminants from the water to the air. For air-stripping towers, these coefficients are estimated using the Onda correlation [Onda et al., 1968, *J. Chem. Eng. Japan*, 1(1), 56–62], which has proven to be surprisingly accurate. Here are the equations for the Onda correlation.

$$k_l = 0.0051 \left( \frac{L_M}{a \mu_L} \right)^{2/3} \left( \frac{\mu_L}{\rho_L D_L} \right)^{-0.5} (a_{tot} d_p)^{0.4} \left( \frac{\rho_L}{\mu_L g} \right)^{-1/3}$$

$$k_g = 5.23 (a_{tot} D_G) \left( \frac{G_M}{a_{tot} \mu_G} \right)^{0.7} \left( \frac{\mu_G}{\rho_G D_G} \right)^{1/3} (a_{tot} d_p)^{-2}$$

$$a = a_{tot} \left\{ 1 - \exp \left[ -1.45 \left( \frac{\sigma_c}{\sigma} \right)^{0.75} (\text{Re})^{0.1} (\text{Fr})^{-0.05} (\text{We})^{0.2} \right] \right\}$$

It is not as bad as it looks. Well, maybe it is. It's kinda bad. But you can do it, really.

Here is what all the terms mean.

Properties of the contaminants:

$D_L$  = diffusivity of the chemical in the liquid phase (i.e., water),  $\text{m}^2/\text{s}$

$D_G$  = diffusivity of the chemical in the gas phase (i.e., air),  $\text{m}^2/\text{s}$

Properties of the air and the water:

$\rho_L$  = density of the liquid phase (i.e., water),  $\text{kg}/\text{m}^3$

$\mu_L$  = viscosity of the liquid phase (i.e., water),  $\text{kg}/(\text{m s})$

$\rho_G$  = density of the gas phase (i.e., air),  $\text{kg}/\text{m}^3$

$\mu_G$  = viscosity of the gas phase (i.e., air),  $\text{kg}/(\text{m s})$

$\sigma$  = surface tension of water,  $\text{kg}/\text{s}^2$

$g$  = gravitational acceleration,  $\text{m}/\text{s}^2$

problem 5 continues →

5. continued

Properties of the air-stripping tower:

- $L_M$  = liquid mass loading rate, i.e., how much water we treat in the tower,  $\text{kg}/(\text{m}^2 \text{ s})$
- $G_M$  = gas mass loading rate, i.e., how much air we blow through the tower,  $\text{kg}/(\text{m}^2 \text{ s})$
- $a$  = wetted specific surface area of the tower packing material,  $1/\text{m}$
- $a_{\text{tot}}$  = overall specific surface area of the tower packing material,  $1/\text{m}$
- $d_p$  = diameter of tower packing material,  $\text{m}$
- $\sigma_c$  = critical surface tension of the packing material,  $\text{N}/\text{m}$  or  $\text{kg}/\text{s}^2$

Dimensionless groups (which are mostly properties of the tower):

- Re = Reynolds number
- Fr = Froude number
- We = Weber number

One of your colleagues has come up with a preliminary design for the air-stripping tower. Based on the preliminary design, we have the following conditions for the tower.

- $L_M$  =  $13.8 \text{ kg}/(\text{m}^2 \text{ s})$
- $G_M$  =  $0.143 \text{ kg}/(\text{m}^2 \text{ s})$
- $d_p$  =  $0.05 \text{ m}$
- $a_{\text{tot}}$  =  $98 \text{ m}^2/\text{m}^3$
- $\sigma_c$  =  $0.033 \text{ kg}/\text{s}^2$
- Re = 141
- Fr = 0.00191
- We = 0.0268
- T =  $25 \text{ }^\circ\text{C}$

We also know that for TCE at this temperature, the diffusion coefficient in water is  $8.5 \times 10^{-10} \text{ m}^2/\text{s}$ , and the diffusion coefficient in air is  $9.8 \times 10^{-6} \text{ m}^2/\text{s}$ .

- a. Estimate/calculate the individual mass-transfer coefficients,  $k_l$  and  $k_g$ , for TCE in the air stripping tower. To do this, you will need to also estimate  $a$ , the wetted specific packing area, because calculating  $k_l$  requires  $a$ . My recommendation is that you set up a spreadsheet rather than doing the calculations by hand, but it is up to you. What is the ratio  $k_g/k_l$ ? – usually we expect this ratio to be between 15 and 150.
- b. Look at the equations for  $k_l$  and  $k_g$ . What is the dependence of  $k_l$  on the aqueous diffusion coefficient,  $D_L$ ? (i.e.,  $k_l$  depends on  $D_L$  raised to what exponent)? What is the dependence of  $k_g$  on the gas diffusion coefficient,  $D_G$ ? Are both the exponents between 0.5 and 1.0 as we would expect? – we will use these dependencies in the next part of the problem.

problem 5 continues →



5. continued

I was able to find published values of the diffusion coefficient for 1,4-dioxane in water. Under dilute conditions, it is right around  $1.1 \times 10^{-9} \text{ m}^2/\text{s}$  at ambient conditions – I found this value published in a couple places. I was not able to find a measured value for the diffusion coefficient of 1,4-dioxane in air. We could calculate it (e.g., using the method of Arnold), but that is a lot of work. I am just going to estimate that it is  $1.3 \times 10^{-5} \text{ m}^2/\text{s}$ .

- c. Estimate/calculate the individual mass-transfer coefficients  $k_l$  and  $k_g$  for 1,4-dioxane in the air-stripping tower. Perform this estimate in the following way. Use the values of  $k_l$  and  $k_g$  that you found for TCE. Then, use the dependence of  $k_l$  and  $k_g$  upon  $D_L$  and  $D_G$  (respectively) that you found in part (b). Estimate the dioxane values of  $k_l$  and  $k_g$  from the TCE values of  $k_l$  and  $k_g$ , using the ratios of the diffusion coefficients.
- d. Would you say that the  $k_l$  values are pretty similar for TCE and 1,4-dioxane? How about the  $k_g$  values? – are they pretty similar, or pretty different?
- e. Estimate/calculate the overall mass-transfer coefficient  $k_{LO}$  for both TCE and 1,4-dioxane. Hint: you will need to look up something (things) in your text book or on-line.
- f. For TCE, estimate/calculate the percentage of the overall mass-transfer resistance that is due to the water and due to the air. (Make sure the percentages add to 100%.) Repeat for 1,4-dioxane. Which phase (air or water) controls the overall mass transfer for TCE? Which phase controls the overall mass transfer for 1,4-dioxane? Are the two chemicals controlled by the same phase? If not, why not?
- g. Estimate/calculate the quantity  $k_{LO} a$  for both TCE and 1,4-dioxane. Specify the units on  $k_{LO} a$ . This quantity is an *apparent rate coefficient* for the transfer of the chemicals from water to air in the air-stripping tower.
- h. When we design the air-stripping tower, we don't want it to be too tall. Tall towers cost more money to build and operate. The height of the tower is proportional to something called the *height of a transfer unit* (HTU). The formula for HTU is
$$\text{HTU} = (L_M/\rho_L) / (k_{LO} a)$$
Estimate/calculate HTU for both TCE and 1,4-dioxane.
- i. Look at the HTU values from part (h) for the two contaminants. Are they similar? Why or why not? Does this answer appear to be consistent with your answer from part (d)? If not, why not? Discuss in terms of *resistance to inter-phase mass transfer*.
- j. Based on your answers to parts (h) and (i), which chemical is likely to control the overall height of the air-stripping tower? Which chemical is more easily amenable to treatment by air stripping? Why? – explain/discuss in terms of the chemical properties of the two contaminants.