Fate & Transport of Chemicals in the Environment

Homework #3 — University of South Florida

Due Monday, Feb. 7, 2022 — Prof J A Cunningham

1. (15 pts)

   (a) Using your text book, look up the aqueous solubility for the following four chemicals: benzene, trichloroethene (also called trichloroethylene, also called TCE), aniline, and phenanthrene. Report the aqueous solubility for these four chemicals in units of mol/L and in units of mg/L.

   (b) Convert the tabulated values of C^{sat} to solubility mole fraction, x^{sat}. Hint: you can assume that the liquid solutions are dilute, even when the chemical is present at its solubility limit. Explain briefly (in a sentence or two) what x^{sat} means.

   We know that Henry's Law is valid when the liquid solution is sufficiently dilute. (For us, "liquid solution" usually means water.) A good rule of thumb is that Henry's Law is valid when the mole fraction x is below 10^{-3} for the chemical of interest.

   (c) Suppose we want to describe the air-water partitioning of the four chemicals benzene, TCE, aniline, and phenanthrene. For which of these chemicals would Henry's Law *always* apply for air-water partitioning? For which of these chemicals would Henry's Law *sometimes* apply for air-water partitioning? Explain (in a few sentences).

2. (15 pts) We know that there are many ways to write Henry's Law, depending on what units of concentration we choose for the liquid phase and for the gas phase. Your text book tabulates Henry's constants with units of L•atm/mol. This assumes that the gas-phase concentration is reported in units of partial pressure (atm) and the aqueous concentration is reported in units of mol/L. I would write it like this:

   $P_i^{air} = H_{PC}\, C_i^{water}$

   where P_i^{air} is the partial pressure of chemical i in the air (atm), C_i^{water} is the concentration of chemical i in the water (mol/L), and H_{PC} is Henry's constant (L•atm/mol).

   Two other ways to write Henry's Law are:

   $C_i^{air} = H_{CC}\, C_i^{water}$ or $y_i = H_{yx}\, x_i$

   in which C_i^{air} is the air-phase concentration (mol/L), y_i is the air-phase mole fraction, and x_i is the aqueous mole fraction. All three formulations are equally valid – they just use different units of concentration. But then the values and units on H are different too!

   (a) Derive the relationship between H_{PC} and H_{CC}. This is not too difficult. What is the relationship between P_i^{air} and C_i^{air}? – if you use this relationship and plug it in to the equations above, you can get the relationship between H_{PC} and H_{CC} pretty easily.

problem 2 continues →

2. continued

   (b) Derive the relationship between H_{yx} and H_{CC}, assuming a temperature of 25 C and a system pressure of 1 atm. I think this one is more difficult than part (a). Start by saying $H_{CC} = C_i^{air}/C_i^{water}$. Then, convert concentration to mole fraction in both the numerator and the denominator. Hint: you might end up using some results from homework #2.

   (c) Look up the value of H_{PC} for 1,1-dichloroethane (DCA) in your text book. Report the value in units L•atm/mol. Then, compute the values of H_{CC} and H_{yx} for DCA. Assume a temperature of 25 C and a system pressure of 1 atm. (The values tabulated in your text book are specific to 25 C and 1 atm, so we must assume these conditions.)

3. (15 pts) Suppose we have some water contaminated with 1,1-dichloroethane (DCA). The concentration of DCA in the water is 12.0 mg/L. We take 70.0 mL of the contaminated water, we put it into a vial, and we seal the vial. The total volume of the vial is 105 mL (i.e., we didn't fill the vial all the way up). The system is allowed to equilibrate at 25 °C. After equilibration, what is the concentration of DCA in the water, in units of mg/L? What is the concentration of DCA in the air? Also estimate the mass of DCA in each phase.

   Hint 1: the total mass of DCA in the vial after equilibrating is the same as the total mass of DCA that we first introduced into the vial. That is, DCA is neither created nor consumed during the equilibration process.

   Hint 2: how is the mass of a chemical in a phase related to the concentration of that chemical in that phase?

   Hint 3: use a result from problem (2).

4. (25 pts) Suppose you built a system in the laboratory in a 1.0-L closed vessel. The system contains 100 g of soil, 500 mL of water, and 450 mL of air. You introduce 100 mg of chlorobenzene into the system and you allow it to equilibrate. The soil in your system is 0.5% organic carbon by mass, i.e., $f_{oc} = 0.005$.

   (a) Look up the octanol-water partition coefficient for chlorobenzene.

   (b) Estimate K_{OC} for chlorobenzene. Be sure the specify the units on K_{OC}. Hint: use Table 3.1 and assume that chlorobenzene is in the "aromatic compounds" category.

   (c) Estimate/calculate K_d for the partitioning of chlorobenzene between your water and your soil. Be sure the specify the units on K_d.

   (d) Look up Henry's constant for chlorobenzene in Table 2.3, and convert it into the H_{CC} form.

   (e) Estimate/calculate the concentration of chlorobenzene in each of the three compartments of your system: water, air, and soil. Hint: the total mass of chlorobenzene equals the sum of the masses in each of the three compartments. The mass in each compartment can be related to the concentration in that compartment.

5. (15 pts) Suppose you had some fathead minnows swimming in your system in problem 5. This is not realistic, because you have only 0.5 L of water in the system, so the minnows wouldn't be very happy; but let's just assume this anyway.

   (a) Estimate/calculate the bioconcentration factor (BCF) for chlorobenzene in fathead minnows. Use the relationship of Veith et al. (1979) from Table 3.3 in your text. Be sure to specify the units on BCF.

   Note: the Veith (1979) equation is pretty good for a one-size-fits-all correlation. The *best* thing is to measure BCF experimentally for your particular chemical of interest and your particular species of fish. But if you don't have time to measure it experimentally, you can get a decent estimate using the Veith (1979) correlation.

   (b) Based on the aqueous concentration that you found in problem (5), what would be the concentration of chlorobenzene in the fish? Report your answer in units of mg/kg. How does it compare to the concentration in the other compartments from problem (5)? Based on this, does uptake by fish seem to be an important consideration when fish are present? – or is it OK to ignore it?

6. (15 pts) You are working in a chemistry laboratory, but unfortunately for you, the ventilation in the lab is poor. Then, to make things even worse, you break the rules of the laboratory by drinking water from an open cup in the lab! This was a bad idea. A large bottle of pure chlorobenzene has been left open in the laboratory, outside of the fume hood. (The violations just keep piling up! Bad ventilation, drinking in the lab, open chemicals outside the hood! Your lab is going to incur some big fines. -- not to mention liver and kidney disease.)

   Assume that the air in the lab is in equilibrium with both the open bottle of chlorobenzene and the water in your cup.

   The temperature in the lab is 25 °C and the pressure is atmospheric.

   (a) Estimate/calculate the concentration of chlorobenzene in the air that you breathe in the lab. Express the concentration as both a mole fraction and as a mass concentration (mg/m^3). Hint: given that the air is in equilibrium with the open bottle of pure chlorobenzene, what do you know about the *partial pressure* of chlorobenzene in the air?

   (b) Estimate/calculate the concentration of chlorobenzene in the water that you drank. Hint: you might have to look something up in your book, or use information from previous problems. For reference, the federal limit on chlorobenzene in publicly supplied drinking water is 0.1 mg/L. How does the concentration in your illicit laboratory water compare to the federal limit in public drinking water?

   (c) How did the chlorobenzene get in the water?