

ENV 6002: Physical & Chemical Principles of Environmental Engineering

Fall 2021
Homework #2
Due Tuesday, Sept. 14, 2021

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Civil & Environmental Engineering
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- (1) (15 pts) In a closed system at 25 °C, a liquid mixture of trichloroethylene (TCE) and tetrachloroethylene (PCE) is in equilibrium with the vapor above it. The vapor consists solely of TCE and PCE, and total pressure of the vapor is 5,280 Pa. Estimate/calculate the mole fractions of TCE and PCE in both the liquid phase and the vapor phase. Hint 1: you can assume that the liquid phase is an ideal solution. Hint 2: look up some data in your text book.
- (2) (25 pts) *Note: this problem is adapted from one in an old chemical engineering text book. I won't tell you which one, but I didn't want to take credit for making up this problem.*
- A mixture of acetonitrile and nitromethane is placed in a cylinder with a moving piston. By moving the piston, we can control the total pressure on the system. The overall composition of the mixture (by moles) is 60% acetonitrile and 40% nitromethane. The temperature of the system is 75 °C; at this temperature, the vapor pressure of acetonitrile is 83.21 kPa, and the vapor pressure of nitromethane is 41.98 kPa. Initially, the pressure on the system is very low, so that the entire mixture is in the vapor phase. Then, we start to compress the system by pressing on the piston.
- (a) We compress the system until the first little drop of liquid forms. This is called the “dew point” because the first drop of “dew” forms. At what pressure does this occur? What are the mole fractions of acetonitrile and nitromethane in the drop of “dew”? Hint 1: we know that $x_{\text{ace}} + x_{\text{nit}} = 1$, and we can use Raoult's Law to substitute in appropriate expressions for x_{ace} and x_{nit} . Hint 2: at the dew point, you know the mole fractions in the *vapor* phase.
- (b) We keep compressing the systems until it is almost completely liquified. Finally, only a very small bubble of vapor remains. This is called the “bubble point”. At what pressure does this occur? What are the mole fractions of acetonitrile and nitromethane in the bubble? Hint 1: it is similar to part (a), but use $y_{\text{ace}} + y_{\text{nit}} = 1$. Hint 2: at the bubble point, you know the mole fractions in the *liquid* phase.
- (3) (5 pts) For a (non-electrolyte) chemical that is partitioning between air and water, over what range of *molar concentration* (mol/L) do you expect Henry's Law to be valid? Explain briefly, in terms of how the aqueous-phase activity coefficient varies with concentration.

(4) (25 pts)

- Using your text book (Table 6-1 or A.6.1), look up the aqueous solubility for the following four chemicals: benzene, trichloroethylene, pyridine, and acenaphthene. Your text book reports aqueous solubility C^{SL} in units of mg/L.
- Convert the tabulated values of C^{SL} to mole fraction, x^{SL} . Hint: you can assume that the liquid solutions are dilute, so that the solution is almost all water.
- If we consider the partitioning of these chemicals between air and water, for which of the four compounds would Henry's Law always be valid, regardless of how much of the chemical is present? Explain very briefly how you decided.
- For whichever chemicals you listed in part (b), estimate/calculate α_i^∞ , H_{yx} , and H_{cc} . Assume that the total pressure of the system is 1 atm, and the temperature is 25 C. Hint: for part of these calculations, you might need to look up something else in the tables.

(5) (15 pts) There are many forms of Henry's Law. One way to write Henry's Law is

$$P_i = H_{PC} C_i^{liq}$$

in which P_i is the partial pressure of chemical i in the vapor phase, C_i^{liq} is the concentration of chemical i in the liquid phase, and H_{PC} is Henry's constant. Let's suppose we have P_i in units of atm and C_i^{liq} in units of mol/m³. Then the units on H_{PC} must be atm•m³/mol.

Another way to write Henry's Law is

$$C_i^{vap} = H_{cc} C_i^{liq}$$

in which C_i^{vap} is the concentration of chemical i in the vapor phase, and H_{cc} is Henry's constant, but with a different value from before. Let's suppose we have C_i^{vap} in units of mol/m³, i.e., the same as C_i^{liq} . Then H_{cc} is dimensionless.

- Determine the relationship between H_{PC} and H_{cc} . Hint: What is the relationship between P_i and C_i^{vap} ? If you write the relationship between P_i and C_i^{vap} , you can substitute it in to one of the forms of Henry's Law given above, and you can pretty quickly derive the relationship between H_{PC} and H_{cc} .
- Your text book tabulates values of H_{PC} for many common organic chemicals at 25 C. These are tabulated in Table 6-1 and in Appendix A.6.1. Look up the value of H_{PC} for 1,1-dichloroethane (DCA) at 25 C. Determine the value of H_{cc} for DCA at 25 C.
- Determine the value of H_{yx} too.

- (6) (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: Use a result from problem (5).

Hint 3: how is the mass of a chemical in a phase related to the concentration of that chemical in that phase?