Fate & Transport of Chemicals in the Environment

Midterm Examination University of South Florida
Wednesday, March 9, 2022 Prof J A Cunningham

Instructions:

1. You may read these instructions, but do not turn the page or begin working until instructed to do so.
2. Answer all questions on your own paper. Please write your name on every page!
3. You are allowed one sheet of 8.5-by-11-inch paper (or A4 paper) with hand-written notes. You may write on both sides of that paper. However, mechanical reproductions (photocopying, laser printing, scanning, etc.) are not allowed; all notes must be hand-written.
4. A calculator is recommended, but it may not be pre-programmed with formulae from the class.
5. Time limit: 65 minutes. Stop working when asked. If you continue working after time has been called, you will be penalized at a rate of 1 point per minute.
6. Show all work and state all assumptions in order to receive maximum credit for your work. If I cannot follow your answer, you will not receive full credit, even if the answer is correct. Furthermore, I can only award partial credit if I can follow what you did.
7. Make sure your answers include units if appropriate. ***Watch your units!!***
8. This exam contains 8 short problems, of which you will answer 6. Each problem is worth 10 points. Thus, the total point value for the exam is 60 points – about one point per minute. Gauge your time accordingly!
9. Use a reasonable number of significant digits when reporting your answers. *You are likely to be graded down* if you report an excessive number of significant digits. In some cases, the problem may indicate the precision to which you should report your answer.
10. Don't cheat. Cheating will result in appropriate disciplinary action according to university policy. Also, cheating indicates a lack of personal integrity.
11. Page 2 of this exam (the back of this page) contains background information, data, constants, and conversion factors that might be helpful to you as you complete the exam.

Exam background:

Decades ago, a drum of used solvents was buried in order to (improperly) dispose of it. Now the drum is corroding, and the solvent mixture is leaking out of the drum and flowing through the ground into a nearby pond. The situation is somewhat reminiscent of the Love Canal disaster. Here is what we know about the site.

- The volume of water in the pond is 2.5×10^5 m^3, the surface area of the pond is 40,000 m^2, and the deepest point of the pond is 9.5 m deep.
- The volume of sediment at the bottom of the pond is 1.0×10^3 m^3, the density of the sediment is 1500 kg/m^3, and the sediment is 10% organic carbon (by mass).
- The temperature of the system is 25 °C.
- One of the solvents in the leaking drum is carbon tetrachloride (CCl_4).
- The molar mass of the solvent mixture is 138 g/mol, the density of the mixture is 1520 g/L, and the mass fraction of CCl_4 in the solvent mixture is 0.20.
- In this system, partitioning of CCl_4 into organic carbon and into fish in the pond are given by
  $\log_{10}(K_{OC}) = 0.88 \log_{10}(K_{OW}) - 0.27$ for K_{OC} in units L/kg
  $\log_{10}(BCF) = 0.94 \log_{10}(K_{OW}) - 0.68$ for BCF in units L/kg

Your text book gives the following properties of CCl_4, which are valid at 25 °C:

Chemical	Molecular weight (molar mass) (g/mol)	Density (g/cm^3)	Aqueous solubility $-\log_{10} C^{SL}$ (mol/L)	Vapor pressure $-\log_{10} P^v$ (atm)	Henry's Law Constant $\log_{10} H_{PC}$ (L•atm/mol)	Octanol-water coefficient $\log_{10} K_{OW}$ (L_{wat}/L_{oct})
CCl_4	153.8	1.59	2.20	0.82	1.38	2.73

Some other potentially useful constants:

Ideal gas constant, R: 8.314 Pa m^3 mol^{-1} K^{-1} = 8.206×10^{-2} atm L mol^{-1} K^{-1}
Molar mass of water, H_2O: 18.01 g/mol
Density of water at 25°C: 0.998 g/mL = 998 kg/m^3
Atomic weights: **C** = 12.011 **Cl** = 35.453 **H** = 1.0079 **N** = 14.007 **O** = 15.999

Potentially useful conversion factors:

Pressure: 1 atm = 760 mm Hg = 760 torr = 101325 Pa
Mass: 1 kg = 1000 g = 1×10^6 mg = 1×10^9 μg
Temperature: 25 °C = 298.15 K
Volume: 1 m^3 = 1000 L = 1×10^6 mL = 1×10^6 cm^3

Answer questions 1–5. Then pick question 6, 7, *or* 8.

1. Show that the *mole fraction* of CCl_4 in the leaking solvent mixture is 0.18 (to two significant digits). Hint: if you choose an arbitrary volume of solvent, such as 1 L, it is not too difficult to calculate the mole fraction of CCl_4 in the solvent. You are given all the information you need on p 2. – but if you don't know how to do this problem, skip it and move on, remembering the final result that the mole fraction of CCl_4 in the solvent is 0.18.

2. Assume that the water in the pond is in equilibrium with the solvent mixture that is leaking into the pond. It is possible to show that, under these conditions, the concentration of CCl_4 in the water is equal to its *aqueous solubility* times its *mole fraction in the solvent mixture*. That is, at equilibrium,
   $C_i^{\text{water}} = x_i^{\text{solvent}} \times C^{\text{SL}}$ where here i denotes CCl_4.
   (You could derive this formula using fugacity relationships, but we won't do that here.)
   Estimate/calculate the concentration of CCl_4 in the aqueous phase, in units of mg/L. Then, convert it to a mole fraction in the aqueous phase, x_i^{water}.

3. Assume the sediment at the bottom of the pond is in equilibrium with the water in the pond. Estimate/calculate the concentration of CCl_4 in the sediment, in units mg/kg.

We think perhaps the CCl_4 is volatilizing out of the pond into the air. We are not sure. We measured the concentration of CCl_4 in the air just above the pond, and the concentration was 17 mg/L.

4. Are the water and the air at equilibrium? If not, which way is the CCl_4 moving – from the air to the water, or from the water to the air? How do you know? Hint: you will need to calculate something before you can answer this question. You can calculate it based on the data provided on p 2.

5. For mass transfer of CCl_4 between the air and the water in the pond, we have estimated that the individual mass-transfer coefficient on the liquid side is $k_L = 1.1 \times 10^{-5}$ m/s. We don't know the individual mass-transfer coefficient k_G on the gas side, but we know the ratio k_G/k_L is somewhere between 20 and 100. Estimate/calculate the overall mass-transfer coefficient, K_L, for mass transfer between air and water. If you make any simplifying assumptions, explain/justify as needed.

Choose question 6, 7, *or* 8.

6. Estimate/calculate the rate at which CCl_4 is entering or exiting the pond across the air-water interface. Report your answer in units g/d, and specify whether the CCl_4 is entering or exiting the pond. Hint #1: write an expression for the mass flux of CCl_4 between air and water. Hint #2: to make the unit conversions easy, notice that 1 mg/L is the same as 1 g/m^3.

7. Use fugacity relationships to derive the equation given in question 2. You will have to assume that the solvent phase is ideal – this is probably OK because many mixtures of organic liquids are close to ideal. Hint: first work in terms of mole fractions, then convert from mole fractions to concentrations.

8. Which phase contains a greater *mass* of CCl_4, the water or the sediment? – by a little, or by a lot? Show the calculations to support your answer. Briefly discuss your result, considering both the chemical properties of CCl_4 and the characteristics of the pond environment.

END OF EXAM