ENV 6002: Physical and Chemical Principles of Environmental Engineering

Fall 2007 | University of South Florida

Midterm Examination | Civil & Environmental Eng.

Mon., Oct. 15, 2007 | 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 in the exam booklet provided, and write your name conspicuously on the exam booklet.
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: 70 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.
7. Make sure your answers include units if appropriate. ***Watch your units!!***
8. This exam contains 3 questions, all with multiple parts. The total point value for the exam is 70 points -- 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.
11. Page 2 of this exam (the back of this page) contains data, constants, and conversion factors that might be helpful to you as you complete the exam.

Properties of ethylbenzene (EB) and 1,2-dichlorobenzene (DCB):

This exam contains questions dealing with the contaminants ethylbenzene (EB) and 1,2-dichlorobenzene (DCB). These are relatively common environmental contaminants. Below is information on the physical-chemical properties of EB and 1,2-DCB at 25 °C.

	Ethylbenzene	1,2-Dichlorobenzene
Atomic formula	C_8H_{10}	$C_6Cl_2H_4$
Molecular weight (g/mol)	106.17	147.0
Liquid density, ρ (g/cm^3)	0.86	1.30
Aqueous solubility, C^{SL} (mole/L)		8.9×10^{-4}
Octanol-water coefficient, K_{ow}		2500
Vapor pressure, P^{sat} (Pa)	1230	200.
Aqueous diffusivity, D (m^2/sec)	1.0×10^{-9}	0.8×10^{-9}

Some other potentially useful constants:

Ideal gas constant, R: 8.314 Pa•m^3•mol^{-1}•K^{-1} = 82.06×10^{-6} atm•m^3•mol^{-1}•K^{-1}

Molecular weight of water, H_2O: 18.01 g/mole

Density of water at 20°C: 0.998 g/mL

Aqueous diffusivity of oxygen at 20°C, D_{O2}^{L}: 2.0×10^{-9} m^2/sec

Henry's constant for oxygen at 20°C, H_{CC}: 30

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

Temperature: 25 °C = 298.15 K

Volume: 1 m^3 = 1000 L = 1×10^6 mL = 1×10^6 cm^3

1. (10 pts) Here is a list of four laws that we discussed in class:

   Clean Water Act (CWA)

   Safe Drinking Water Act (SDWA)

   Resource Conservation and Recovery Act (RCRA)

   Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

   For each of the five concepts below, indicate which one of these four laws is most pertinent. Each is worth two points.

   a. National Priorities List
   b. antidegradation policy
   c. National Pollutant Discharge Elimination System (NPDES)
   d. secondary standard
   e. joint, several, and retroactive

Exam continues →

2. (20 pts) Consider an environment that contains both air and water. It is at atmospheric pressure and is at a temperature of 25 °C. Some ethylbenzene (an aromatic hydrocarbon found in petroleum) has been spilled into the environment, and it now contaminates both the water and the air. You may assume that the environment is at equilibrium. Answer the following questions.

a. (2 pts) Under the scenario described above, what is the relationship between the fugacity of ethylbenzene in the water phase ($\hat{f}_{EB}^{water}$) and the fugacity of ethylbenzene in the air phase ($\hat{f}_{EB}^{air}$)?

You measure the concentration of ethylbenzene in the air and find that the mole fraction of ethylbenzene in the air is $y = 0.00012$. Then, you measure the concentration of ethylbenzene in the water and find it to be $C = 1.68$ mg/L.

b. (5 pts) Estimate/calculate the mole fraction of ethylbenzene in the water.
c. (5 pts) Estimate/calculate the activity coefficient, γ, of ethylbenzene in the water. Hint: use your answer from part (a) and proceed from there.
d. (3 pts) Based on your answer to part (c), would you consider ethylbenzene to be hydrophilic, slightly hydrophobic, moderately hydrophobic, or strongly hydrophobic? Explain briefly -- one or two sentences should probably suffice.
e. (5 pts) Estimate/calculate the aqueous solubility of ethylbenzene in units of mg/L.

Exam continues →

3. (40 pts) This problem deals with the partitioning of 1,2-dichlorobenzene (1,2-DCB) in the environment at 25 °C.

   a. (5 pts) Calculate/estimate the value of Henry's constant (in its dimensionless H_{cc} form) for 1,2-DCB at 25 °C.
   b. (5 pts) Calculate/estimate the distribution coefficient, K_d, for the partitioning of 1,2-DCB onto sediment that is 8.0% organic carbon and has a density of 1700 kg/m^3. Report your K_d value in units of [(g DCB per kg of sediment)/(g DCB per m^3 water)].
   c. (3 pts) For the same sediment as in part (b), estimate the dimensionless sorption coefficient, K_p. Report your answer with units [(g DCB per m^3 sediment)/(g DCB per m^3 water)].
   d. (4 pts) Calculate/estimate the bioconcentration factor for 1,2-DCB, assuming that aquatic organisms are 25% lipid matter.

Suppose that an unknown quantity of 1,2-DCB is spilled into a lake environment. Estimated volumes of compartments in this lake environment are:

7×10^6 m^3 water;

7×10^8 m^3 air;

2×10^4 m^3 sediment (with density 1700 kg/m^3 and 8.0% organic carbon); and

4 m^3 aquatic organisms (with 25% lipid matter).

You may assume that the system has reached equilibrium, and that all compartments have a temperature of about 25 °C.

   e. (7 pts) Which of the following statements is correct?
      i. The concentration of 1,2-DCB (expressed as g/m^3) is highest in the water phase.
      ii. The concentration of 1,2-DCB is highest in the air phase.
      iii. The concentration of 1,2-DCB is highest in the sediment phase.
      iv. The concentration of 1,2-DCB is highest in the biota (the organisms).
      v. There is not enough information available to know which compartment has the highest concentration.

      Briefly explain <u>why</u> you selected your choice. You will be graded on both your selection and your reasoning.

Exam continues →

3. continued

f. (8 pts) Which of the following statements is correct?

   i. Most of the DCB mass is in the water phase.

   ii. Most of the DCB mass is in the air phase.

   iii. Most of the DCB mass is in the sediment phase.

   iv. Most of the DCB mass is in the biota (the organisms).

   v. There is no single phase that contains most of the DCB mass.

   vi. There is not enough information available to know which compartment(s) contains most of the DCB mass.

   Briefly explain why you selected your choice. You will be graded on both your selection and your reasoning.

g. (8 pts) Briefly discuss the partitioning of 1,2-DCB in this environment. Where does most of the DCB mass end up, and why? Did you find that the compartment with the highest DCB concentration is also the compartment with the highest DCB mass? If not, why not? Explain in terms of the relevant *chemical properties* and *environmental characteristics*.

END OF EXAMINATION

1. Match phrases with the appropriate law.

(a) National Priorities List : CERCLA
list of "Superfund Sites" most in need of clean-up

(b) antidegradation policy : Clean Water Act
the antidegradation policy is the third part of a water quality standard

(c) NPDES : Clean Water Act
system that requires a permit for discharge to a surface water

(d) secondary standard : Safe Drinking Water Act
non-enforceable standard for drinking water, based on aesthetics.

(e) joint, several, and retroactive : CERCLA
describes the liability at a contaminated site

2. Ethylbenzene in the environment

(a) Fugacity relationship

$$\hat{f}_{EB}^{water} = \hat{f}_{EB}^{air}$$

(b) Mole fraction of ethylbenzene in water

$$\frac{1.68 \text{ mg ethylbenz.}}{\text{L solution}} * \frac{1 \text{ g}}{1000 \text{ mg}} * \frac{1 \text{ mole EB}}{106.17 \text{ g EB}} * \frac{1 \text{ L solution}}{55.56 \text{ moles soln}}$$

$$X_{EB} = 2.85 \times 10^{-7}$$

(c) Estimate the activity coefficient

From part a: $\hat{f}_{EB}^{water} = \hat{f}_{EB}^{air}$

$$X_i \gamma_i P_i^{sat} = y_i P$$

$$\therefore \gamma_i = \frac{y_i P}{X_i P_i^{sat}} = \frac{(0.00012)(1 \text{ atm})(101325 \text{ Pa/atm})}{(2.85 \cdot 10^{-7})(1230 \text{ Pa})}$$

$$\gamma_{EB} = 34{,}700$$

(d) see next page

(e) Estimate aqueous solubility

If $X_i^{SL} < 10^{-3}$, then $\gamma = 1/X^{SL}$

Thus $X^{SL} = 1/\gamma$ assuming $X^{SL} < 10^{-3}$

$X^{SL} = 2.88 \times 10^{-5}$ [dilute solution ... OK]

$$C^{SL} = \frac{2.88 \times 10^{-5} \text{ moles EB}}{\text{mole solution}} * \frac{55.56 \text{ moles soln}}{\text{L soln}} * \frac{106.17 \text{ g EB}}{1 \text{ mole EB}} * \frac{1000 \text{ mg}}{\text{g}}$$

$$C^{SL} = 170 \text{ mg/L}$$

2. .. continued

(d) Based on γ, is ethylbenzene hydrophilic or hydrophobic?

$\gamma = 34{,}700$: meaning ethylbenzene is 34,700 times "less comfortable" in water than it is in a pure solution of ethylbenzene. I think this value is high enough to consider ethylbenzene "strongly hydrophobic." However, there are chemicals with significantly higher values of γ, so by comparison, it would be acceptable to consider ethylbenzene only "moderately hydrophobic." Personally, I'd say "strongly hydrophobic" is warranted.

3. Partitioning of 1,2-DCB

(a) Calculate H_{cc}

$$H_{cc} = \left[P^{sat} / RT \right] \div C^{SL}$$

Given $P^{sat} = 200 \text{ Pa}$

$T = 25 \text{ C} = 298 \text{ K}$

$C^{SL} = 8.9 \times 10^{-4} \text{ mole/L} = 0.89 \text{ mole/m}^3$

$$H_{cc} = \frac{(200 \text{ Pa}) / (8.314 \text{ J/mol}\cdot\text{K})(298.15 \text{ K})}{(0.89 \text{ mole/m}^3)} = 0.091$$

$H_{cc} = 0.091$

(b) Calculate K_d in units $\frac{g/kg}{g/m^3}$.

Given $K_{ow} = 2500$

$\therefore K_{oc} = (0.63 \times 10^{-6})(2500) = 0.00158 \frac{g/g}{g/m^3}$

$= 1.58 \frac{g/kg}{g/m^3}$

$K_d = f_{oc} K_{oc} = (0.080)(1.58 \frac{g/kg}{g/m^3})$

$K_d = 0.126 \text{ (g DCB/kg sediment)/(g DCB/m}^3 \text{ water)}$

(c) Calculate K_p

$$K_p = K_d \cdot \rho_s$$

$$K_p = 0.126 \frac{\text{g DCB / kg sediment}}{\text{g DCB / m}^3 \text{ water}} \cdot 1700 \frac{\text{kg sediment}}{\text{m}^3 \text{ sediment}}$$

$$K_p = 214 \frac{\text{g DCB/m}^3 \text{ sediment}}{\text{g DCB/m}^3 \text{ water}}$$

3. Continued

(d) Calculate bioconcentration factor, BCF

$$BCF = f_{lipo} K_{ow}$$

$$= (0.25)(2500)$$

$$BCF = 625$$

(e) Which compartment has highest concentration of DCB?

iv. The DCB concentration is highest in the biota.

How do we know?

H_{cc}, K_p, and BCF are all <u>concentration ratios.</u>

$$H_{cc} = \frac{\text{Conc. in air}}{\text{Conc. in water}} = 0.091$$

$$K_p = \frac{\text{Conc. in sediment}}{\text{Conc. in water}} = 214$$

$$BCF = \frac{\text{Conc. in biota}}{\text{Conc. in water}} = 625$$

Therefore, we know that the concentrations follow this order:

$$C_{DCB}^{air} < C_{DCB}^{water} < C_{DCB}^{sediment} < C_{DCB}^{biota}$$

(f) Where is most of the DCB mass?

Recall that a mass ratio is a concentration ratio times a volume ratio.

$$\frac{M_{DCB}^{air}}{M_{DCB}^{water}} = H_{cc} \cdot \frac{V^{air}}{V^{water}} = (0.091) \frac{7 \times 10^8 \ m^3}{7 \times 10^6 \ m^3} = 9.1$$

$$\frac{M_{DCB}^{sediment}}{M_{DCB}^{water}} = K_p \cdot \frac{V^{sediment}}{V^{water}} = (214) \frac{2 \times 10^4 \ m^3}{7 \times 10^6 \ m^3} = 0.61$$

3... continued

(f) continued

$$\frac{M_{DCB}^{biota}}{M_{DCB}^{water}} = 625 \cdot \frac{V^{biota}}{V^{water}} = 0.00036$$

Thus the <u>mass</u> ratios are as follows:

$$M_{DCB}^{biota} : M_{DCB}^{sediment} : M_{DCB}^{water} : M_{DCB}^{air} = 0.00036 : 0.61 : 1 : 9.1$$

Thus, overall, about 85% of the mass is in the <u>air</u> phase.

ii. Most of the DCB mass is in the air phase.

(g) Explain in terms of chemical properties and environmental characteristics.

Concentrations : $C^{biota} > C^{sediment} > C^{water} > C^{air}$

Mass : $M^{air} > M^{water} > M^{sediment} > M^{biota}$

The trends are exactly opposite! Interesting.

DCB is a hydrophobic compound -- relatively high K_{ow} -- so we would expect it to partition into the sediment and the biota. This is what we see when we look at the concentrations. However, the <u>volume</u> of the <u>air</u> phase is so large that, on a <u>mass</u> basis, most of the mass is in the air. The vapor pressure is not high, but it is high enough that, when coupled with a large air volume, 85% of the mass ends up in the air. Similarly, the relatively high water volume means that about 9% of the DCB mass is in the water, despite its relatively low aqueous solubility.