

ENV 6519: Physical and Chemical Processes in Environmental Engineering

Spring 2011

Examination

Thurs., March 24, 2011

University of South Florida

Civil & Environmental Eng.

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Instructions:

1. You may read these instructions, but do not turn the page or begin working until instructed.
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. **Choose any two of the three problems.** If you attempt all three, you will be given credit for the two on which you score highest. However, this is probably not a good strategy; you are probably better off concentrating on two problems and trying to do them well, rather than attempting all three.
9. The total point value for the exam is 70 points -- one point per minute. Gauge your time accordingly!
10. 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.
11. Don't cheat. Cheating will result in appropriate disciplinary action according to university policy. More importantly, cheating indicates a lack of personal integrity.
12. 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. I recommend that you read page 2 carefully, especially the background information, as it is likely that you will need some of that information to complete the problems on the exam.
13. Additional pages, photocopied from your course text, are provided to give you additional information. You might or might not find the information useful.

Background Information

1,2-Dichloroethane (1,2-DCA) is used as a solvent and as a chemical intermediate in the synthesis of other commercially important chemicals. However, 1,2-DCA is both toxic and carcinogenic, and therefore it has a federal drinking-water MCL of 5 mg/L. In this exam, we will consider a contaminated water stream that contains 1,2-DCA at a concentration of 200 $\mu\text{g/L}$. We are trying to treat the water to its drinking-water standard, i.e., 5 $\mu\text{g/L}$. You may assume a temperature of 25 $^{\circ}\text{C}$. The flow rate of the contaminated water is 130 gal/min = 0.0082 m^3/s .

Properties of 1,2-DCA at 25 $^{\circ}\text{C}$:

| | |
|--|---|
| Molecular formula: | $\text{C}_2\text{H}_4\text{Cl}_2$ |
| Molecular weight: | 98.96 g/mole |
| Liquid density: | $1.25 \text{ g/cm}^3 = 1250 \text{ kg/m}^3$ |
| Vapor pressure, P^{sat} : | |
| Aqueous solubility: | |
| Octanol-water partition coefficient: | $10^{1.46} = 29$ |
| Reaction rate constant with $\cdot\text{OH}$: | $2.0 \times 10^8 \text{ L}/(\text{mol}\cdot\text{s})$ according to text Table 8-8 |
| Heat of vaporization, ΔH : | not given in your book's Table 14-3 |

Potentially useful constants:

| | |
|---|---|
| Ideal gas constant, R : | $8.314 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 82.06 \times 10^{-6} \text{ atm}\cdot\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ |
| Gravitational acceleration, g : | 9.81 m/s^2 |
| Molecular weight of water, H_2O : | 18.01 g/mole |
| Density of water at 25 $^{\circ}\text{C}$: | $0.9970 \text{ g/mL} = 997 \text{ kg/m}^3$ |
| Viscosity of water at 25 $^{\circ}\text{C}$: | $0.890 \times 10^{-3} \text{ Pa}\cdot\text{sec}$ |
| Density of air at 25 $^{\circ}\text{C}$: | 1.18 kg/m^3 |
| Viscosity of air at 25 $^{\circ}\text{C}$: | $1.85 \times 10^{-5} \text{ Pa}\cdot\text{sec}$ |

Potentially useful conversion factors:

| | |
|--------------|---|
| Pressure: | $1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 101325 \text{ Pa}$ |
| Mass: | $1 \text{ kg} = 1000 \text{ g} = 10^6 \text{ mg} = 10^9 \mu\text{g}$ |
| Temperature: | $25 \text{ }^{\circ}\text{C} = 298.15 \text{ K}$ |
| Volume: | $1 \text{ m}^3 = 1000 \text{ L} = 10^6 \text{ mL} = 10^6 \text{ cm}^3$ |
| Other : | $1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ kg}/(\text{m}\cdot\text{sec}^2)$ |

Atomic Masses:

| | | | |
|--------------------|--------------------|-------------------|-------------------|
| H = 1.008 g/mole | C = 12.011 g/mole | N = 14.007 g/mole | O = 15.999 g/mole |
| Cl = 35.453 g/mole | Br = 79.904 g/mole | | |

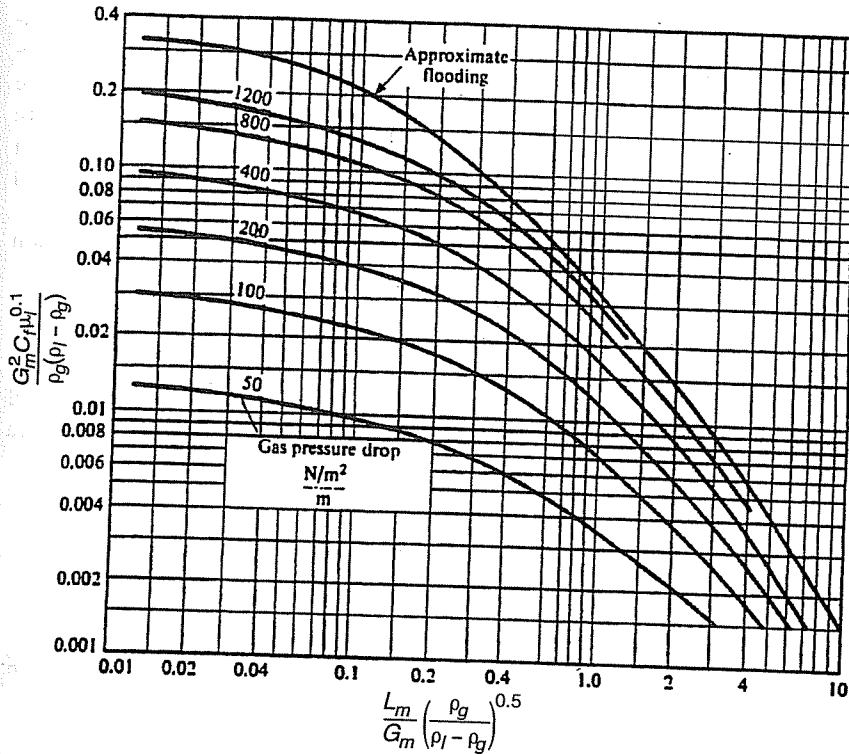


Figure 14-19

Generalized Eckert gas pressure drop and liquid and gas loading correlation for random packed tower (Eckert, 1961; Treybal, 1980).

Table 8-11Important elementary reactions involved in $\text{H}_2\text{O}_2/\text{O}_3$ and $\text{H}_2\text{O}_2/\text{UV}$ processes at near-neutral pH

| Number | Reactions | Rate Constants at 25°C, $\text{M}^{-1} \text{s}^{-1}$ | References |
|---|--|---|------------|
| Reactions Specifically for $\text{H}_2\text{O}_2/\text{O}_3$ Process | | | |
| 1 | $\text{HO}_2^- + \text{O}_3 \xrightarrow{k_1} \text{O}_3^- \cdot + \text{HO}_2 \cdot$ | $k_1 = 2.8 \times 10^6$ | a |
| 2 | $\text{OH}^- + \text{O}_3 \xrightarrow{k_2} \text{HO}_2^- + \text{O}_2$ | $k_2 = 70$ | a |
| 3 | $\text{O}_2^- \cdot + \text{O}_3 \xrightarrow{k_3} \text{O}_3^- \cdot + \text{O}_2$ | $k_3 = 1.6 \times 10^9$ | b |
| 4 | $\text{O}_3^- \cdot + \text{H}^+ \xrightarrow{k_4} \text{HO}_3 \cdot$ | $k_4 = 5.2 \times 10^{10}$ | b |
| 5 | $\text{HO}_3 \cdot \xrightarrow{k_5} \text{HO} \cdot + \text{O}_2$ | $k_5 = 1.1 \times 10^5 \text{ s}^{-1}$ | b |
| 6 | $\text{O}_3 + \text{R} \xrightarrow{k_6} \text{Products}$ | k_6 —see Table E-2, Appendix E | |
| Reactions Specifically for $\text{H}_2\text{O}_2/\text{UV}$ Process | | | |
| | | $r_{\text{UV}, \text{H}_2\text{O}_2} = r_{\text{HO} \cdot} / 2 = -\phi_{\text{H}_2\text{O}_2} / 0 f_{\text{H}_2\text{O}_2} (1 - e^{-A})$ | |
| | | $A = \frac{2.303b(\epsilon_{\text{H}_2\text{O}_2} C_{\text{H}_2\text{O}_2} + \epsilon_{\text{R1}} C_{\text{R1}} + \epsilon_{\text{NOM}} C_{\text{NOM}})}{\epsilon_{\text{H}_2\text{O}_2, 254 \text{ nm}}}$ | |
| 7 | $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{HO} \cdot$ | $f_{\text{H}_2\text{O}_2} = 2.303b(\epsilon_{\text{H}_2\text{O}_2} C_{\text{H}_2\text{O}_2} + \epsilon_{\text{HO}_2^-} C_{\text{HO}_2^-}) / A$ $\epsilon_{\text{H}_2\text{O}_2, 254 \text{ nm}} = 17.9 \sim 19.6 \text{ M}^{-1} \text{ cm}^{-1}$ $\phi_{\text{H}_2\text{O}_2} = \phi_{\text{HO}_2^-} = 0.5$ | |
| 8 | $\text{R} + h\nu \rightarrow \text{products}$ | $r_{\text{UV}, \text{R}} = -\phi_{\text{R}} / 0 f_{\text{R}} (1 - e^{-A})$ $f_{\text{R}} = 2.303b \epsilon_{\text{R}} C_{\text{R}} / A$ | |
| Reactions Common for Both $\text{H}_2\text{O}_2/\text{O}_3$ and $\text{H}_2\text{O}_2/\text{UV}$ Process | | | |
| 9 | $\text{HO} \cdot + \text{HO}_2^- \xrightarrow{k_9} \text{OH}^- + \text{HO}_2 \cdot$ | $k_9 = 7.5 \times 10^9$ | c |
| 10 | $\text{HO} \cdot + \text{H}_2\text{O}_2 \xrightarrow{k_{10}} \text{H}_2\text{O} + \text{HO}_2 \cdot$ | $k_{10} = 2.7 \times 10^7$ | d |
| 11 | $\text{HO} \cdot + \text{HCO}_3^- \xrightarrow{k_{11}} \text{CO}_3^- \cdot + \text{H}_2\text{O}$ | $k_{11} = 8.5 \times 10^6$ | d |
| 12 | $\text{HO} \cdot + \text{R} \xrightarrow{k_{12}} \text{products}$ | k_{12} —see Table E-4, Appendix E | |
| 13 | $\text{HO} \cdot + \text{NOM} \xrightarrow{k_{13}} \text{products}$ | $k_{13} = 3 \times 10^8 \text{ to } 4.5 \times 10^8 \text{ (average } 3.9 \times 10^8) \text{ L/mole NOM carbon-s}$ | e |

(continued)

Table 8-11*(Continued)*

| Number | Reactions | Rate Constants at 25°C, M ⁻¹ s ⁻¹ | References |
|------------------------------------|--|---|------------|
| Acid Dissociation Constants | | | |
| 14 | $\text{H}_2\text{CO}_3^* \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ | $\text{p}K_{a1} = 6.3$ | f |
| 15 | $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ | $\text{p}K_{a2} = 10.3$ | f |
| 16 | $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ | $\text{p}K_{a3} = 14$ | f |
| 17 | $\text{H}_2\text{O}_2 \rightleftharpoons \text{H}^+ + \text{HO}_2^-$ | $\text{p}K_{a5} = 11.75$ | g |
| 18 | $\text{HO}_2 \cdot \rightleftharpoons \text{H}^+ + \text{O}_2^- \cdot$ | $\text{p}K_{a6} = 4.8$ | a |

References: (a) Staehelin and Hoigne, 1982; (b) Buhler et al., 1984; (c) Christensen et al., 1982; (d) Buxton and Greenstock, 1988; (e) Westerhoff et al., 1999; (f) Stumm and Morgan, 1981; (g) Behar et al., 1970.

1. (35 pts) Imagine that you are going to use **adsorption onto activated carbon** to remove 1,2-DCA from water at 25 °C.

Suppose you ran batch isotherm experiments with your contaminated water and Calgon F300 activated carbon. You let a known volume of contaminated water equilibrate with a known mass of activated carbon, and then you measured/estimated the concentration of 1,2-DCA in the water and adsorbed to the carbon. You repeated this four times with different mass-to-volume ratios. Below is a table of the data you gathered from the four experiments.

| Experiment # | Equil. conc. of 1,2-DCA in water ($\mu\text{g/L}$) | Equil. conc. of 1,2-DCA on carbon ($\mu\text{g/g}$) |
|--------------|--|---|
| 1 | 15.9 | 109. |
| 2 | 31.6 | 190. |
| 3 | 63.1 | 331. |
| 4 | 126. | 574. |

- a. (6 pts) From these data, show that the Freundlich parameter $1/n$ is equal to 0.80 for equilibrium sorption of 1,2-DCA onto Calgon F300. Then estimate/calculate the Freundlich parameter K_F . Be sure to specify proper units!

Now suppose you built a fixed-bed pressure vessel filled with Calgon F300 granular activated carbon (GAC) to treat the contaminated water. The GAC contactor is 3 m long and has a diameter of 2 m. The bulk density of the GAC in the contactor is $\rho_f = 480 \text{ kg/m}^3$.

- b. (6 pts) Estimate the empty-bed contact time (EBCT) and the superficial velocity (v_0). Do the values appear reasonable?
- c. (6 pts) Imagine a scenario in which, as the contaminated water travels through your contactor, the mass-transfer zone is infinitesimally thin. Under this overly-optimistic condition, how many bed volumes would you be able to treat before 1,2-DCA breaks through? What would be the carbon usage rate (in units of g GAC per m^3 water)?
- d. (6 pts) Unfortunately, when you actually treated the contaminated water with your GAC contactor, you observed that your carbon usage rate was 1.6 times as large as the theoretical minimum that you estimated in part (c). Based on this information, estimate/calculate the length of the mass transfer zone, L_{MTZ} . Hint: how many bed volumes did you treat before breakthrough?

problem 1 continues -->

1. continued

- e. (6 pts) If you make your contactor longer, but keep everything else the same, your carbon usage rate will go down. How long must you make your contactor in order that the carbon usage rate be no more than 20% above the theoretical minimum? Hint: you may assume that the constant-pattern assumption is valid, which enables you to use your estimated L_{MTZ} from part (d).
- f. (5 pts) Assuming that all the numbers above are realistic, do you think that adsorption onto activated carbon is a good way to treat water contaminated with 200 $\mu\text{g/L}$ of 1,2-DCA? Why or why not?

2. (35 pts) Imagine that you are investigating whether **air stripping** is a good treatment technique for the removal of 1,2-DCA from water at 25 °C. You will use packed-tower aeration to treat the contaminated water.

One of your colleagues designed and built an air stripping tower to treat the contaminated water. Your colleague gave you this information about the tower.

Tower diameter, $d = 1.0$ m

Packing type = 2" plastic saddles

Packing diameter, $d_p = 0.0508$ m

Packing factor, $C_f = 20$

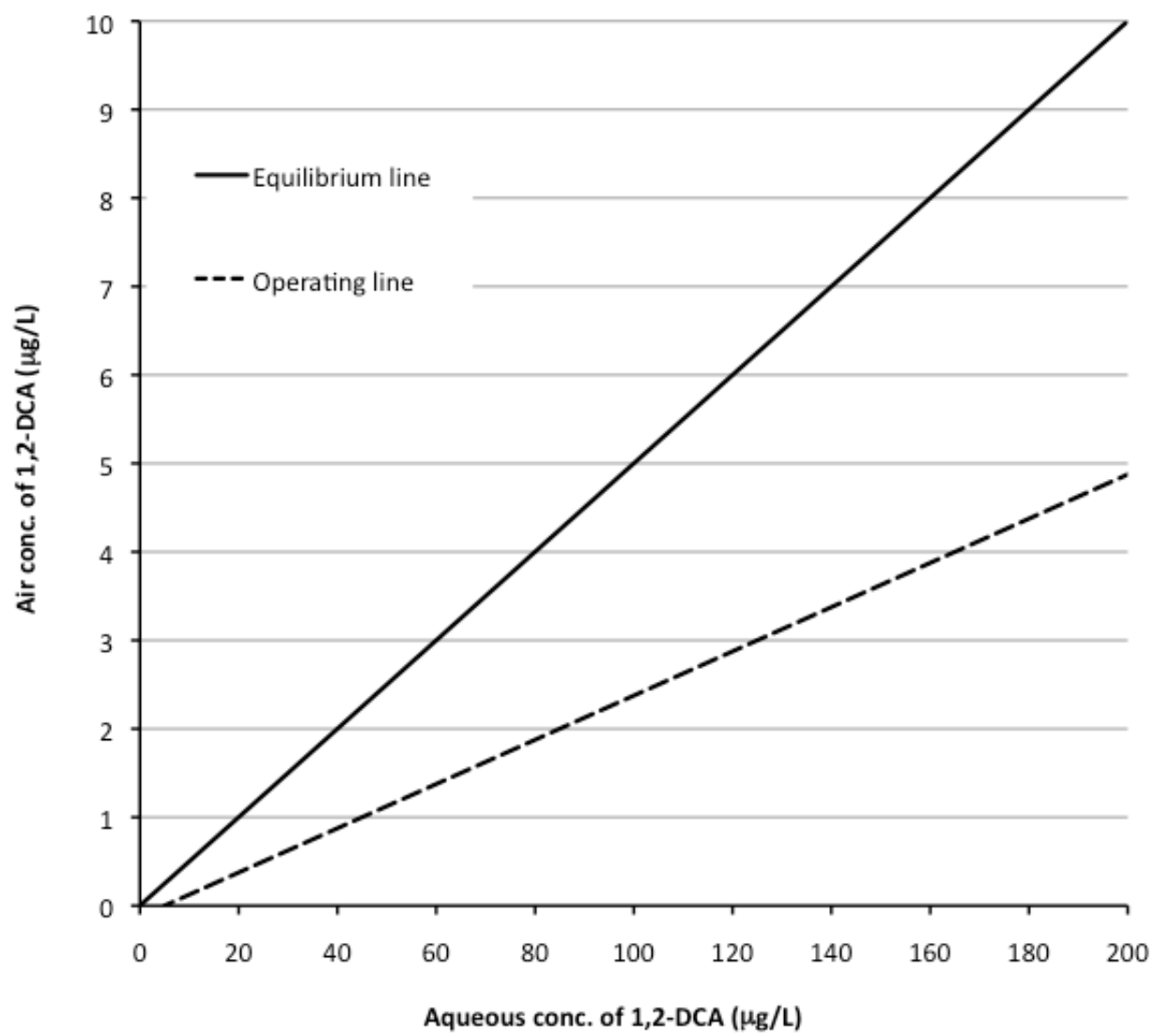
Liquid-side mass transfer coefficient, estimated by Onda correlation, $k_L = 2.45 \times 10^{-4}$ m/sec

Gas-side mass transfer coefficient, estimated by Onda correlation, $k_G = 1.10 \times 10^{-2}$ m/sec

Wetted surface area of packing, estimated by Onda correlation, $a_w = 58.3$ m²/m³

In addition, your colleague provided you with an *operating diagram* for the air stripping unit, which is shown on the following page.

- (5 pts) Estimate/calculate Henry's constant, H , for 1,2-DCA at a temperature of 25 °C. Report H in its dimensionless form. Hint: use the operating diagram.
- (5 pts) Estimate/calculate the value of the stripping factor, S , for 1,2-DCA in this air stripping unit. Hint: use the operating diagram.
- (13 pts) Estimate/calculate the height of the tower, L . Hint: estimate HTU and NTU to help you estimate L .
- (7 pts) Estimate/calculate the liquid loading rate, L_M , and the gas loading rate, G_M , both in units of kg/(m²·s). Also estimate/calculate the air-to-water ratio, Q_a/Q . Based on these estimates, do you expect to have a problem with pressure drop in the tower? Explain. (You can do more elaborate calculations if you wish, but you only have about 7 minutes to spend on this problem, so don't get carried away.)
- (5 pts) Does air stripping appear to be a good way to treat water contaminated with 200 µg/L of 1,2-DCA? Why or why not?



3. (35 pts) Imagine that you are employing **oxidation by ozone with hydrogen peroxide** for the removal of 1,2-DCA from water.

Suppose that the process is taking place in a completely-mixed flow reactor (CMFR) through which the contaminated water flows. Ozone is bubbled into the bottom of the reactor, and hydrogen peroxide is added to the contaminated water just before it enters the reactor. This enhances the formation of the $\cdot\text{OH}$ radical to destroy the 1,2-DCA.

- (6 pts) Imagine that you want to be able to reach your treatment objective (5 $\mu\text{g/L}$) with a residence time of no greater than $\tau = 20$ min. What concentration of hydroxyl radicals, $[\cdot\text{OH}]$, must you maintain in the reactor?
- (6 pts) Now suppose that, instead of treating the water in a single CMFR with $\tau = 20$ min, you will use four CMFRs in series, each with a residence time of $\tau = 5$ min. Thus the overall residence time remains the same as in part (a). If we assume that the concentration of hydroxyl radicals, $[\cdot\text{OH}]$, is the same in all four reactors, what concentration is required?
- (3 pts) Based only on the concentration of hydroxyl radicals (i.e., ignoring considerations like cost of construction), which configuration do you recommend, that in part (a) or that in part (b)? Explain briefly (a sentence or two).

Now let's try to decide if it is feasible to maintain the hydroxyl radical concentration that you estimated. Suppose that the conditions in the reactor(s) are approximately the following.

Temperature, $T = 25$ °C

Henry's constant for ozone gas at 25 °C, $H_{\text{PC}} = 89.1$ atm·L/mol

Overall mass-transfer rate constant for ozone, $K_L a = 4.0 \times 10^{-4}$ /sec

pH of contaminated water = 7.0

Concentration of bicarbonate in the water, $[\text{HCO}_3^-] = 183$ mg/L = 3.0×10^{-3} mol/L

Concentration of dissolved organic carbon, $[\text{NOM}] = 0.24$ mg/L = 2.0×10^{-5} mol/L

Concentration of peroxide in the reactor, $[\text{H}_2\text{O}_2] = 0.42$ mg/L = 1.22×10^{-5} mol/L

Concentration of ozone in the reactor, $[\text{O}_3] = 6.8 \times 10^{-4}$ mol/L

- (10 pts) Estimate/calculate the partial pressure of ozone in the gas stream that would be required to maintain the desired concentration of hydroxyl radicals. Is it a reasonable value? Explain briefly (a sentence or two). Hint: equation 8-189 from the text says the following.

$$[\cdot\text{OH}] = \frac{K_L a \left(\frac{P_{\text{O}_3}}{H_{\text{O}_3}} - [\text{O}_3] \right)}{k_9 [\text{HO}_2^-] + k_{10} [\text{H}_2\text{O}_2] + k_{11} [\text{HCO}_3^-] + k_{12} [\text{R}] + k_{13} [\text{NOM}]}$$

problem 3 continues -->

3. continued

- e. (5 pts) Suppose in part (d) you said that the required partial pressure of ozone was not reasonable. Suppose you wanted to cut the partial pressure of ozone in half, but you still want to maintain your desired concentration of hydroxyl radicals in the reactor. You might be able to do this if you decreased the quenching of hydroxyl radicals. What chemical species in the water would you remove in order to decrease the quenching? Approximately how much removal would be necessary? (You won't be able to get an exact answer without iterative calculations, so just make your best estimate.)
- f. (5 pts) Does oxidation by ozone with hydrogen peroxide appear to be a good way to treat water contaminated with 200 $\mu\text{g/L}$ of 1,2-DCA? Why or why not?

END OF EXAMINATION