ENV 6519: Physical and Chemical Processes for Groundwater Remediation

Spring 2019	University of South Florida
Examination	Civil & Environmental Eng.
Mon., April 1, 2019	J. A. Cunningham

Instructions:

1. You may read these instructions, but do not turn the page or begin working until instructed.
2. If an exam booklet (e.g., a "blue book") is provided, answer all questions in the exam booklet provided, and write your name conspicuously on the exam booklet. If no booklet is provided, use your own paper, write your name on each page, and staple them together before submitting.
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. ***Answer any two***.
9. If you attempt all 3 questions, make it clear which two you want me to grade. Otherwise, I will select the two which I think I can grade the fastest; this is not likely to work to your advantage.
10. The total point value for the exam is 100 points. Gauge your time accordingly!
11. 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.
12. Don't cheat. Cheating will result in appropriate disciplinary action according to university policy. More importantly, cheating indicates a lack of personal integrity.
13. Pages 2–3 of this exam contain 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.
14. Additional pages, photocopied from your course text, are provided to give you additional information (pp 3–5 of this exam). You might or might not find the information useful.
15. Hint #1: When you are working on these problems, answer each part of the question *in order*. That is, answer part (a) before you do part (b); answer part (b) before you do part (c); etc. You may need the answers from the earlier parts in order to answer the later parts.
16. Hint #2: If you don't know how to do one of the parts of the problem, just write "I do not know how to do this, so I will assume an answer of _____," and then pick a *reasonable* value. That will enable you to move on and answer the later parts of the question.

Background Information

Your supervisor at your consulting firm needs you to fix a big mistake made by one of your co-workers. A major client hired your company to design three possible treatment systems to clean up their contaminated groundwater. The design flow rate for the treatment systems is 100 gallons per minute (equivalent to 0.0063 m^3/s), and the groundwater is at a temperature of 18 °C. The groundwater contains 1,1-dichloroethane (DCA) at a concentration of 700 μg/L, and the water must be treated to a concentration of 7 μg/L (99.0% removal).

The problem is that your co-worker thought he was supposed to treat 1,1-dichloroethene (DCE), not 1,1-dichloroethane (DCA). So all of his designs are probably wrong. When the mistake was discovered, your co-worker was so embarrassed that he quit his job and moved to a remote village in Bhutan. Now you need to check all the designs to see if they are OK to send to the client, and possibly you need to re-design some of the treatment systems. Remember: DCE is the erroneous contaminant; DCA is the contaminant you actually should treat ("E" for erroneous, "A" for actual).

Properties of DCE and DCA at 18 °C:

	1,1-DCE	**1,1-DCA**
Molecular formula	$C_2H_2Cl_2$	$C_2H_4Cl_2$
Molar mass (g/mole)	96.94	98.96
Liquid density (g/cm^3)	1.22	1.18
Vapor pressure, P^{sat} (Pa)	57,200	22,300
Aqueous solubility, C^{SL} (g/L)	2.5	5.1
Octanol-water partition coefficient	$10^{1.48} = 30$	$10^{1.79} = 62$
Index of refraction (at 20 °C)	1.4249	1.4164
Reaction rate coefficient with $^{\bullet}OH$ (L/(mol•s))	6.8×10^{9}	1.1×10^{8}
Heat of vaporization, ΔH_{vap} (kJ/mol)	30.4	28.7

Second-order reaction rate coefficients from 2nd edition of Crittenden text; heats of vaporation from Staudinger & Roberts (2001); Indeces of refraction from CRC Handbook; other data from 2nd edition of Schwarzenbach text (Environmental Organic Chemistry), adjusted for temperature.

Potentially useful constants:

Ideal gas constant, *R*:	$8.314\ Pa\cdot m^3\cdot mol^{-1}\cdot K^{-1} = 82.06\times10^{-6}\ atm\cdot m^3\cdot mol^{-1}\cdot K^{-1}$
Gravitational acceleration, *g*:	$9.81\ m/s^2$
Molecular weight of water, H_2O:	18.01 g/mole
Density of water at 18 °C:	0.9986 g/mL = 998.6 kg/m^3
Viscosity of water at 18 °C:	1.06×10^{-3} Pa•sec = 1.06×10^{-3} kg/(m•sec)
Density of air at 18 °C:	1.21 kg/m^3
Viscosity of air at 18 °C:	1.82×10^{-5} Pa• sec = 1.82×10^{-5} kg/(m•sec)

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

Potentially useful conversion factors:

Pressure:	1 atm = 760 mm Hg = 760 torr = 101325 Pa
Mass:	1 kg = 1000 g = 10^6 mg = 10^9 μg
Temperature:	25 °C = 298.15 K
Volume:	1 m^3 = 1000 L = 10^6 mL = 10^6 cm^3
	1 gal = 3.785 L
Other:	1 Pa = 1 N/m^2 = 1 $kg/(m•s^2)$
	1 J = 1 N•m = 1 $kg•m^2/s^2$

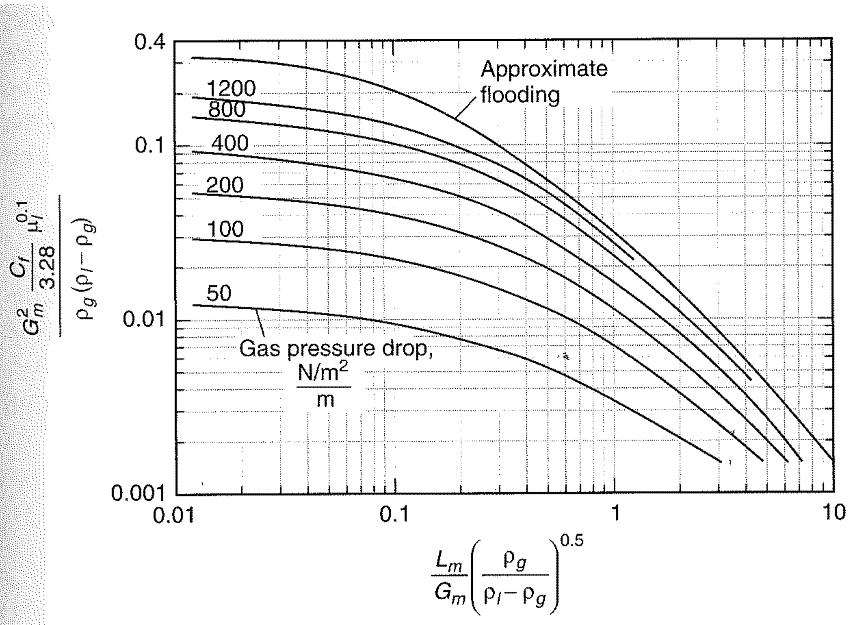
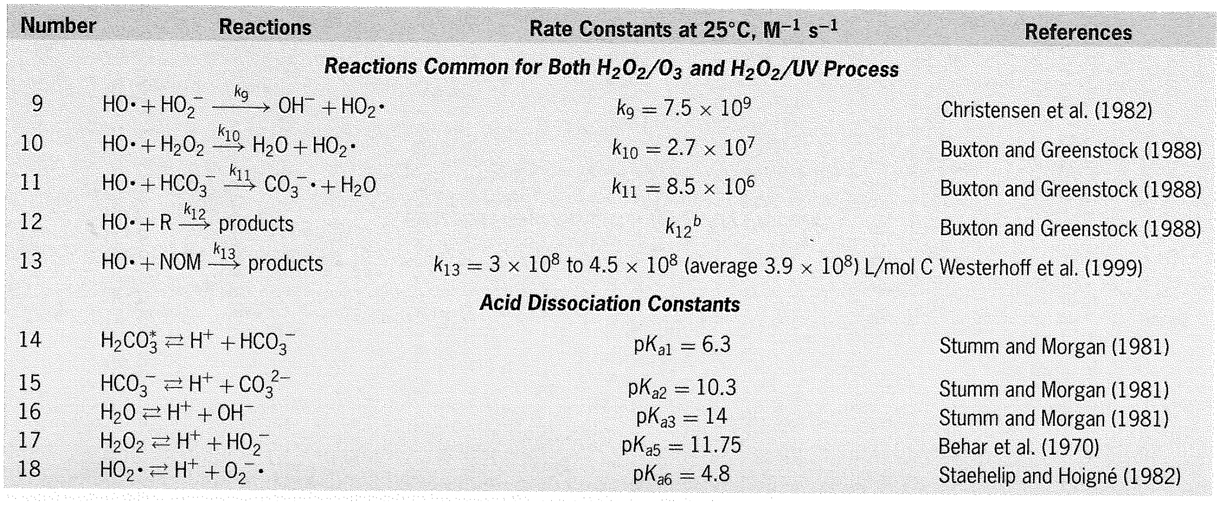


Figure 14-21
Generalized Eckert gas pressure drop and liquid and gas loading correlation in SI units for random packed tower. The coefficient 3.28 is a conversion factor when the packing factor in SI units (m^{-1}) is used because the Eckert diagram was originally drawn in English units. (Adapted from Eckert, 1961; Treybal, 1980).

Table 18-5 *(Continued)*



Number	Reactions	Rate Constants at 25°C, M^{-1} s^{-1}	References
		Reactions Common for Both H_2O_2/O_3 and H_2O_2/UV Process	
9	$HO\cdot + HO_2^- \xrightarrow{k_9} OH^- + HO_2\cdot$	$k_9 = 7.5 \times 10^9$	Christensen et al. (1982)
10	$HO\cdot + H_2O_2 \xrightarrow{k_{10}} H_2O + HO_2\cdot$	$k_{10} = 2.7 \times 10^7$	Buxton and Greenstock (1988)
11	$HO\cdot + HCO_3^- \xrightarrow{k_{11}} CO_3^-\cdot + H_2O$	$k_{11} = 8.5 \times 10^6$	Buxton and Greenstock (1988)
12	$HO\cdot + R \xrightarrow{k_{12}}$ products	$k_{12}{}^b$	Buxton and Greenstock (1988)
13	$HO\cdot + NOM \xrightarrow{k_{13}}$ products	$k_{13} = 3 \times 10^8$ to 4.5×10^8 (average 3.9×10^8) L/mol C	Westerhoff et al. (1999)
		Acid Dissociation Constants	
14	$H_2CO_3^* \rightleftarrows H^+ + HCO_3^-$	$pK_{a1} = 6.3$	Stumm and Morgan (1981)
15	$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$	$pK_{a2} = 10.3$	Stumm and Morgan (1981)
16	$H_2O \rightleftarrows H^+ + OH^-$	$pK_{a3} = 14$	Stumm and Morgan (1981)
17	$H_2O_2 \rightleftarrows H^+ + HO_2^-$	$pK_{a5} = 11.75$	Behar et al. (1970)
18	$HO_2\cdot \rightleftarrows H^+ + O_2^-\cdot$	$pK_{a6} = 4.8$	Staehelip and Hoigné (1982)

Table 18-2

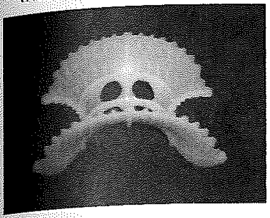
Reaction rate constants and half lives for degradation of selected inorganic and organic species by hydroxyl radicals[a]

Compound	HO· Rate Constant, L/mol · s	Half-Life, min		
		$[HO\cdot] = 10^{-9}$ M	$[HO\cdot] = 10^{-10}$ M	$[HO\cdot] = 10^{-11}$ M
Inorganics				
Ammonia	9.0×10^{7}	0.13	1.3	13
Bicarbonate	8.5×10^{6}	1.4	14	140
Bromide	1.1×10^{10}	0.001	0.01	0.1
Carbonate	3.9×10^{8}	0.03	0.3	3
Chloride	4.3×10^{9}	0.003	0.03	0.3
Iron(II)	3.2×10^{8}	0.04	0.4	4
Hydrogen peroxide	2.7×10^{7}	0.43	4.3	43
Manganese(II)	3.0×10^{7}	0.39	3.9	39
Ozone	1.1×10^{8}	0.11	1	11
Organics				
Acetate ion	7.0×10^{7}	0.2	2	17
Acetone	1.1×10^{8}	0.11	1.1	11
Atrazine	2.6×10^{9}	0.004	0.04	0.44
Benzene	7.8×10^{9}	0.001	0.01	0.1
Chloroacetic acid	4.3×10^{7}	0.3	2.7	27
Chlorobenzene	4.5×10^{9}	0.003	0.03	0.3
Chloroform	5.0×10^{6}	2	23	231
2-Chlorophenol	1.2×10^{10}	0.001	0.01	0.1
Formate ion	2.8×10^{9}	0.004	0.0	0
Geosmin	$(1.4 \pm 0.3) \times 10^{10}$	0.00083	0.0083	0.083
Methyl ethyl ketone	9.0×10^{8}	0.01	0.1	1
Methyl *tert*-butyl ether	1.6×10^{9}	0.01	0.1	1
MIB	$(8.2 \pm 0.4) \times 10^{9}$	0.0014	0.014	0.14
Natural organic matter	1.4 to 4.5×10^{8}	0.03	0.3	3.0
Oxalic acid	1.4×10^{6}	8	83	825
Oxalic ion	1.0×10^{7}	1	12	116
p-Dioxane	2.8×10^{9}	0.004	0.04	0.4
Phenol	6.6×10^{9}	0.002	0.02	0.2
Tetrachloroethylene	2.6×10^{9}	0.004	0.04	0.4
1,1,1-Trichloroethane	4.0×10^{7}	0.3	3	29
1,1,2-Trichloroethane	1.1×10^{8}	0.11	1	11
Trichloroethylene	4.2×10^{9}	0.003	0.03	0.3
Trichloromethane	5.0×10^{6}	2	23	231
Urea	7.9×10^{5}	15	146.2	1462
Vinyl chloride	1.2×10^{10}	0.001	0.01	0.1

[a] Additional values are available in the electronic Table E-4 at the website listed in App. E.

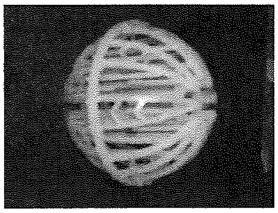
Source: Adapted from Buxton and Greenstock (1988), Lal et al. (1988), and Mao et al. (1991).

Intalox Saddles



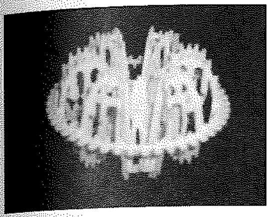
d_p	5.08 cm (2.0 in.)	7.62 cm (3.0 in.)
C_f	69 m^{-1} (21 ft^{-1})	52 m^{-1} (16 ft^{-1})
a_t	98 m^{-1} (30 ft^{-1})	66 m^{-1} (20 ft^{-1})

Jaeger Tri-Packs



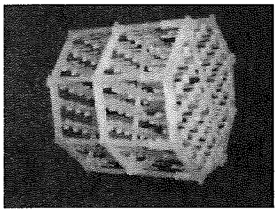
d_p	5.08 cm (2.3 in.)	8.89 cm (3.5 in.)
C_f	52 m^{-1} (16 ft^{-1})	39 m^{-1} (12 ft^{-1})
a_t	157 m^{-1} (48 ft^{-1})	125 m^{-1} (38 ft^{-1})

Tellerettes (Type K)



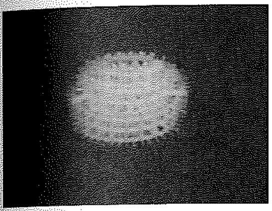
	No. 2	No. 3
d_p	5.08 cm (2.0 in.)	7.62 cm (3.0 in.)
C_f	36 m^{-1} (11 ft^{-1})	30 m^{-1} (9 ft^{-1})
a_t	52 m^{-1} (28 ft^{-1})	72 m^{-1} (22 ft^{-1})

Lantec Q-PAC



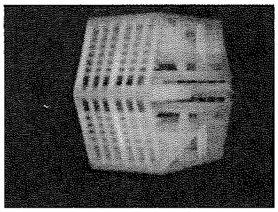
d_p	8.89 cm (3.5 in.)	
C_f	23 m^{-1} (7 ft^{-1})	
a_t	98 m^{-1} (30 ft^{-1})	

Lantec NUPAC



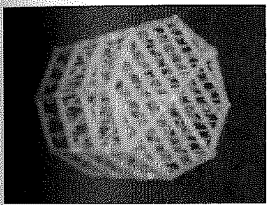
d_p	6.32 cm (2.5 in.)	11.4 cm (4.5 in.)
C_f	53 m^{-1} (16 ft^{-1})	26 m^{-1} (8 ft^{-1})
a_t	180 m^{-1} (55 ft^{-1})	131 m^{-1} (40 ft^{-1})

Lantec LANPAC



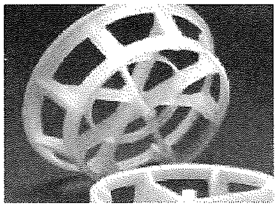
d_p	5.84 cm (2.3 in.)	8.89 cm (3.5 in.)
C_f	69 m^{-1} (21 ft^{-1})	46 m^{-1} (14 ft^{-1})
a_t	223 m^{-1} (68 ft^{-1})	144 m-1 (44 ft-1)

Lantec LANPAC-XL



d_p	8.89 cm (3.5 in.)	
C_f	33 m^{-1} (10 ft^{-1})	
a_t	242 m^{-1} (74 ft^{-1})	

Plastic rings



d_p	5.08 cm (2.0 in.)	7.62 cm (3.0 in.)
C_f	82 m^{-1} (25 ft^{-1})	30 m^{-1} (9 ft^{-1})
a_t	108 m^{-1} (33 ft^{-1})	72 m-1 (22 ft-1)

Critical surface tension depends on material, for polypropylene, $\sigma_c = 0.033$ N/m

Figure 14-12
Typical examples of polyethylene packing materials used in air-stripping towers and their physical characteristics.

1. (50 pts) Your colleague designed a system to treat the contaminated groundwater stream by the process of **adsorption** onto a fixed bed of **granular activated carbon (GAC)**. We are not sure what type of activated carbon he planned on using, but we did find the following information in the notes that he left in his office.

   GAC grain internal porosity, $\varepsilon_p = 0.57$ Intergranular porosity of bed, $\varepsilon = 0.40$
   Bulk density of carbon in the bed, $\rho_f = 540$ kg/m^3
   Polanyi $\sigma = 1.00$
   Freundlich $1/n = 0.689$
   Minimum carbon usage rate (UR) = 54 g GAC / m^3 water treated

   a. (8 pts) Assume that the numbers above are correct for DCE. Estimate/calculate the adsorbed concentration of DCE on the GAC, i.e., the adsorbed concentration in equilibrium with the contaminated water. Report your answer in units of μg/g. Hint: use the reported minimum carbon usage rate.
   b. (6 pts) Estimate/calculate the Freundlich K_F value for DCE. Report your answer in units of (μg/g)/(μg/L)$^{1/n}$. Hint: use your answer from part (a).
   c. (14 pts) Assuming that the numbers above are correct for DCE, estimate/calculate the Freundlich parameters for DCA. Report your estimate of K_F in units of (μg/g)/(μg/L)$^{1/n}$. Hint 1: use Polanyi theory. Hint 2: Calculate $1/n$ first, then calculate K_F.
   d. (7 pts) Estimate/calculate the minimum carbon usage rate for DCA. Is it better or worse than the value originally estimated by your colleague? By how much?
   e. (5 pts) Estimate/calculate the number of bed volumes you could treat before the GAC is exhausted (for DCA treatment). Assume the mass-transfer zone is infinitesimally thin.
   f. (5 pts) Does it seem that GAC is a viable technology for treating the actual contaminated water? Explain briefly – just a sentence or two should suffice.
   g. (5 pts) If you had built this system *without* catching your co-worker's error, and then you started operating the system, would the actual treatment cost be *higher* or *lower* than what you had promised the client? Why? Would the client be happy, or unhappy?

2. (50 pts) Your colleague designed a system to treat the contaminated groundwater stream by the process of **air stripping** (packed tower aeration). Keep in mind that your colleague thought he was designing a tower for DCE removal, not DCA removal. We are missing a lot of the details of his design, but we did find the following information in the notes that he left in his office.

Packing type = 2-inch plastic rings
Stripping factor $S = 6.0$
Effluent concentration $C_e = 7\ \mu g/L$
Henry's constant $H = 0.92$
Required height of packing material $L = 5.0$ m

From the Onda correlation: $k_L = 2.5\times10^{-4}$ m/s, $k_G = 2.3\times10^{-3}$ m/s, $a_w = 59.9\ m^2/m^3$

a. (3 pts) Assume that the numbers above are correct for removal of DCE. What air flow rate would give the indicated stripping factor? Report your answer in m^3/s.

b. (5 pts) Estimate/calculate the *number of transfer units* (NTU) for the tower designed by your colleague for DCE removal.

c. (3 pts) Estimate/calculate the *height of a transfer unit* (HTU) for the tower designed by your colleague. Hint: you are given the required height of the packing material, L.

d. (8 pts) Estimate/calculate the cross-sectional area of the tower designed by your colleague. Hint: use the HTU that you calculated in part c.

So now we know the air flow rate, the tower diameter, and the packing height that your colleague had planned on using for his tower. That might work just fine for removal of DCE, but now we need to see if that design would work for DCA.

e. (7 pts) Estimate/calculate Henry's constant, H, for DCA.

f. (6 pts) Suppose that we use the same tower diameter and air flow rate as designed by your colleague. In that case, it is probably OK to assume that k_L, k_G, and a_w are the same for DCE and DCA. Why is this OK? What chemical property or properties affect k_L, k_G, and a_w? Are these properties pretty similar or pretty different for DCE and DCA?

g. (8 pts) Re-calculate S and HTU for DCA. Hint: you will need to re-calculate K_La.

h. (10 pts) Suppose we tried to use the same L as designed by your colleague. Estimate/calculate the NTU that would be available (based on L and HTU). Then, estimate/calculate the <u>effluent concentration of DCA</u>, C_e, that we could achieve with this design. (Hint: use the NTU.) Can we meet the treatment objective of $7\ \mu g/L$?

i. BONUS – NOT REQUIRED -- UP TO 5 ADDITIONAL POINTS
If you had built this system according to your co-worker's design, *without* catching his error, and then you started operating the system, would the actual performance be *better* or *worse* than what you had promised the client? Why? (i.e., what is different about DCE and DCA?) Would the client be happy, or unhappy?

[There is actually much more I wanted to ask you, but this question is long enough already!]

3. (50 pts) Your colleague designed a system to treat the contaminated groundwater stream by the process of **advanced oxidation by ozone and peroxide**. The design is based on a single-stage completely mixed flow reactor (CMFR). Ozone is bubbled in to the bottom of the reactor, and peroxide is dosed into the contaminated groundwater just before it enters the reactor. We are missing a lot of the details of your co-worker's design, but we did find the following information in the notes that he left in his office.

   Reactor volume $V = 10\ \mathrm{m}^3$

   Ozone delivery: $K_L\,a = 7.0\times10\text{–}4\ \mathrm{s}^{-1}$, $P_{O3} = 0.04$ atm, H_{PC} (at 18 °C) = 70 atm•L/mol

   Estimated/predicted concentrations in the reactor:

   $[\mathrm{H_2O_2}] = 2.1\times10^{-4}$ M $[\mathrm{HCO_3^-}] = 1.6\times10^{-3}$ M $[\mathrm{DOC}] = 9.0\times10^{-6}$ M $[\mathrm{O_3}] = 1.4\times10^{-5}$ M

   $$[\bullet\mathrm{OH}] = \frac{K_L a\, P_{O3}\ /\ H_{PC}}{k_{10}[\mathrm{H_2O_2}] + k_{11}[\mathrm{HCO_3^-}] + k_{13}[\mathrm{DOC}] + k_{12}[\mathrm{DCE}]}$$

   $$[\mathrm{DCE}] = \frac{7.2\times10^{-6}\ \mathrm{M}}{1 + k_1^{\mathrm{app}}\tau}$$ (because the influent conc. of DCE is 7.2×10^{-6} M)

   a. (18 pts) Assume that the equations and the numbers given above would be correct for removal of DCE. Estimate/calculate the concentration of DCE exiting the reactor. Report your answer in both mol/L and μg/L. Would the treatment objective of 7 μg/L be achieved? Hint 1: use the equations given above. Hint 2: If you look up second-order reaction rate coefficients for 25 °C, assume they are valid at 18 °C. Hint #3: the algebra might get messy, but it is do-able. I used an iterative approach to solve the messy algebra, but there are probably other approaches.

   b. (7 pts) Based on the concentration of DCE you found in part (a), estimate/calculate the concentration of hydroxyl radicals, [•OH], in the reactor. Report your answer in mol/L. Does this look like a reasonable value? Hint: depending on how you solved part (a), you might have already calculated this concentration.

   c. (8 pts) Now let's account for the fact that we actually should be removing DCA, not DCE. For now, let's assume that the concentration of hydroxyl radicals from part (b) would still be correct for DCA. Estimate/calculate the concentration of DCA that would exit the reactor. Report your answer in both mol/L and μg/L. Would the treatment objective of 7 μg/L be achieved?

   d. (4 pts) Compare your results from part (a) to your results from part (c). Does the system work equally well for DCE and DCA? Why or why not? Explain briefly.

problem 3 continues →

3. continued

   e. (8 pts) Let's re-think the concentration of hydroxyl radicals, [$^{\bullet}$OH]. When you made your estimate in part (b), you were thinking that we were treating DCE. But now we know we are treating DCA. Based on that, do you think your estimate from part (b) is too high, too low, or just about right? Explain. (If you want, you can re-calculate [$^{\bullet}$OH] based on DCA, but this is not strictly necessary.) Based on this, will the system performance be *better* than what you had assumed in part (c), *worse* than what you had assumed in part (c), or *about the same* as what you had assumed in part (c)? Do you want to modify your estimate of the DCA concentration exiting the system?

   f. (5 pts) If you had built this system according to your co-worker's design, *without* catching his error, and then you started operating the system, would the actual performance be *better* or *worse* than what you had promised the client? Why? (i.e., what is different about DCE and DCA?) Would the client be happy, or unhappy?

END OF EXAMINATION