DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
UNIVERSITY OF CALIFORNIA, BERKELEY
CE 111 FALL 2011

MIDTERM ONE

Name: SOLUTIONS

The exam is worth 100 points and has four problems. Make sure to read each question carefully, and allocate your time wisely. You must show all steps of any calculations you perform. Put a box around each final answer. Use the paper provided. You may use the backside of the paper if you need more room. Make sure your name is written on the top of each sheet.

Problem	Score
1	
2	
3	
4	
Total	

Other details about the format of the exam (same as what was sent to you by email):

- As always, you are expected to conduct your own work. The seats are very close together, but **you MAY NOT look at your neighbors exams**. Mi will be monitoring the classroom for wandering eyes.
- All you need to bring with you is a pencil, eraser, and calculator.
- Please fill the seats in the middle of each row first, otherwise students that arrive late will have to interrupt an entire row to get to a middle seat.
- The exams will be passed out when you arrive to class, but you may not look at them.
- Everyone will start working on the exam promptly at 11:10.
- You can tear off the top sheet which has the equations. You do not need to hand this sheet in at the end.
- You will not be allowed to ask any questions during the exam, because it is not possible for students to get out of their seats without disrupting their neighbors. If you feel you do not understand part of a question, re-read it carefully several times. If you still don't understand, make an assumption that allows you to continue and write a short note explaining what your assumption is.
- The exam will end promptly at 12:00. When Mi announces that the exam has ended, **everyone must put down their pencils immediately.** It is not fair if some students stop and others don't. Mi will be very strict about this. You will hand your exam to the person at the end of your row, and then Mi will come and pick them up from each row.

1. (25 points) Consider the composition of a groundwater that is in equilibrium with $CaCO_{3(s)}$, the main component of limestone. The composition of all the species in the water is not known, but the concentration of calcium is measured to be $[Ca^{2+}] = 0.1$ mM, and the pH is measured to be 8.5. You may assume that there is no air present. The acid dissociation constants for carbonate species are: $pK_{a1} = 6.35$, $pK_{a2} = 10.33$, and the solubility constant for $CaCO_{3(s)}$ is $K_{sp} = 5 \times 10^{-9}\ M^2$.

   a. What is the dominant species that contributes to the alkalinity of the water under these conditions?

   HCO_3^-

   b. Calculate the alkalinity of the water in eq/L.

   $$Alk = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$$

   $$Alk \sim [HCO_3^-] \text{ at pH } 8.5$$

   $$[H^+] = 10^{-8.5}$$

   $$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 5 \times 10^{-9}\ M^2$$

   $$[CO_3^{2-}] = \frac{K_{sp}}{[Ca^{2+}]} = \frac{5 \times 10^{-9}\ M^2}{0.1 \times 10^{-3}\ M} = 5.00 \times 10^{-5}\ M$$

   $$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

   $$[HCO_3^-] = \frac{[H^+][CO_3^{2-}]}{K_{a2}} = \frac{(10^{-8.5}\ M)(5.00 \times 10^{-5}\ M)}{10^{-10.33}\ M}$$

   $$[HCO_3^-] = 3.38 \times 10^{-3}\ M$$

   $$\boxed{Alk \sim 3.38 \times 10^{-3}\ eq/L}$$

   or

   $$Alk = 10^{-6.5} + 3.38 \times 10^{-3} + 2(5.00 \times 10^{-5}) - 10^{-8.5} = \boxed{3.48 \times 10^{-3}\ eq/L}$$

c. If this water is pumped out of the ground and exposed to the atmosphere, will the pH increase, decrease, or stay the same? Explain why in 1 sentence.

Decrease, because CO_2 will dissolve as $H_2CO_3^*$, which is an acid.

d. If this water is pumped out of the ground and exposed to the atmosphere, will the alkalinity increase, decrease, or stay the same? Explain why in 1 sentence.

Stay the same, b/c adding $H_2CO_3^*$ does not change the alkalinity

2. (25 points) MTBE (methyl tert-butyl ether), which has the molecular formula $C_5H_{12}O$, was added to gasoline in California for several decades in an effort to reduce air pollution. Unfortunately, MTBE migrated into many groundwater supplies through leaky storage tanks. The California Department of Public Health has established primary and secondary MCLs for MTBE in drinking water of 13 ppb and 5 ppb, respectively (represented as mass fraction).

a. What is the difference between a primary and secondary MCL? Explain in one sentence.

Primary MCL - designed to protect health

Secondary MCL - designed to maintain aesthetic quality of water (e.g. taste and odor)

b. A groundwater in Monterey County has a concentration of 3.6×10^{-6} mol/L MTBE. What percent removal is necessary to just meet the primary MCL?

Convert 13ppb to mol/L

MW MTBE = 5(12) + 12(1) + 16 = 88 g/mol

$$5 \text{ ppb} = \left(\frac{13 \times 10^{-6} \text{ g MTBE}}{\text{L}}\right)\left(\frac{\text{mol}}{88 \text{ g}}\right) = 1.48 \times 10^{-7} \text{ mol/L}$$

$$\% \text{ removal} = \left(\frac{3.6 \times 10^{-6} - 1.48 \times 10^{-7}}{3.6 \times 10^{-6}}\right) = \boxed{95.9\%}$$

OR

Convert 3.6×10^{-6} mol/L to ppb:

$$\left(3.6 \times 10^{-6} \text{ mol/L}\right)\left(\frac{88 \text{ g}}{\text{mol}}\right) = 3.17 \times 10^{-4} \text{ g/L} = 317 \text{ ppb}$$

$$\% \text{ removal} = \frac{317 - 13}{317} = \boxed{95.9\%}$$

OR $$\frac{3.17 \times 10^{-4} \text{ g/L} - 1.3 \times 10^{-5} \text{ g/L}}{3.17 \times 10^{-4} \text{ g/L}} = \boxed{95.9\%}$$

c. If the odor threshold for MTBE is 20 ppb_v, will someone be able to smell MTBE in air that is in equilibrium with the contaminated water in part b (3.6 x 10^{-6} mol/L MTBE)? $K_{H, MTBE}$ = 1.8 M/atm, and the total air pressure is 1 atm.

$$K_H = \frac{C}{P}$$

$$P = \frac{C}{K_H} = \frac{3.6 \times 10^{-6}\ M}{1.8\ M/atm} = 2.0 \times 10^{-6}\ atm$$

1st way

Convert P to volume fraction (= mol fraction)

$$\text{mol fraction} = \frac{n_{MTBE}}{n_{air}} = \frac{\frac{P_{MTBE}V}{RT}}{\frac{P_{air}V}{RT}} = \frac{P_{MTBE}}{P_{air}} = 2.0 \times 10^{-6} = \underline{2.0\ ppm}$$

2nd way

Partial pressure = $X\ P_{Tot}$

$$X = \frac{P_{MTBE}}{P_{TOT}} = 2.0 \times 10^{-6} = \underline{2.0\ ppm}$$

3rd way

2.0 ppm > 20 ppb

Yes you can smell the MTBE

3. (25 points) MTBE can be degraded by aerobic bacteria that are naturally present in soil. The degradation rate is first-order with respect to the MTBE concentration. An experiment was conducted in which the concentration of MTBE decreased from 2.1 mg/L to 3.5 μg/L in 2 days.

   a. Calculate the first-order rate constant for the degradation of MTBE under these conditions.

$$k = -\frac{1}{t}\ln\frac{C}{C_o} = -\left(\frac{1}{2d}\right)\left(\ln\frac{2.1\times10^{-3}}{3.5\times10^{-6}}\right)$$

$$\boxed{k = 3.2\ d^{-1}}$$

   b. How long would it take to reduce the concentration of MTBE by 99.9%? If you are not confident about the rate constant you determined in part a, you may use a value of 5 d^{-1}.

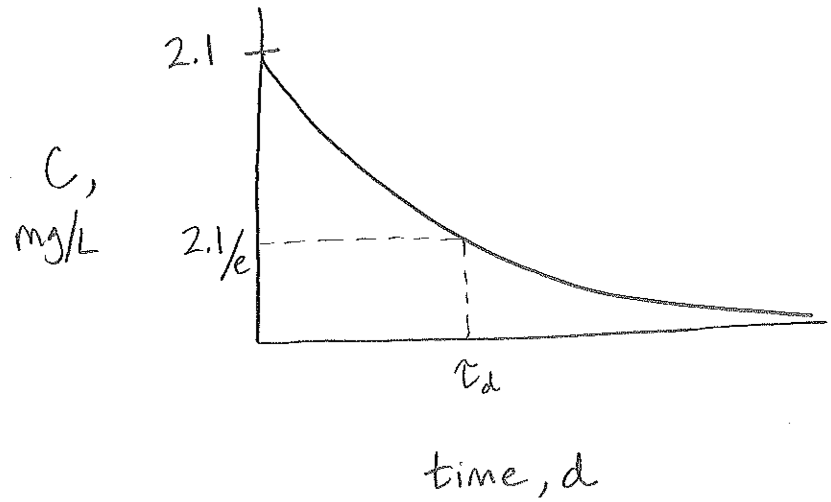
$$t = -\frac{1}{k}\ln\frac{C}{C_o} \quad \text{where} \quad \frac{C}{C_o} = \frac{1}{1000}$$

$$t = -\frac{1}{(3.2\ d^{-1})}\ln\left(\frac{1}{1000}\right) = \boxed{2.16\ d}$$

OR

$$t = -\frac{1}{5d^{-1}}\ln\frac{1}{1000} = \boxed{1.38\ d}$$

c. Draw a graph showing the concentration of MTBE as a function of time. Label the characteristic time on the graph.



$\tau_d = \frac{1}{k} = 0.31$ or 0.2

4. (25 points) Acid mine drainage is released from many abandon metal and coal mining sites. The acidic drainage is due to the activity of bacteria, which oxidize metal sulfides. One example reaction is the oxidation of iron sulfide, shown below. All species in the reaction are shown, but the reaction is not balanced. Note that the iron is not oxidized or reduced in this reaction.

$$\overset{2}{a}FeS_2 + \overset{7}{b}O_2 + \overset{2}{c}H_2O \rightarrow \overset{2}{d}Fe^{2+} + \overset{4}{e}SO_4^{2-} + \overset{4}{f}H^+$$

a. What is the oxidation state of sulfur in FeS_2 and SO_4^{2-}?

FeS_2 : -1

SO_4^{2-} : +6

b. Balance the redox reaction (determine the values of a, b, c, d, e, f)

Stoichiometry: $a = d$, $e = 2a$ $a=2$, $d=2$, $e=4$

balance e⁻s:

S: $2(-1) \longrightarrow 2(+6) = 14e^-$ transferred

O: $7(0) \longrightarrow 7(-2) = 14e^-$ transferred

$b = \frac{7}{2}a = 7$

balance charge: $f = 2d - 2e = 2(2) - 2(4) = -4$ $f=4$

check stoichiometry:

	LHS	RHS
Fe	2	2
S	4	4
O	16	16
H	4	4

$c=2$

a=2	a=1
b=7	b=7/2
c=2	c=1
d=2	d=1
e=4	e=2
f=4	f=2

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

$$FeS_2 + \frac{7}{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$