DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
UNIVERSITY OF CALIFORNIA, BERKELEY
CE 111 FALL 2016

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 rules/expectations (same as what I posted on bCourses):

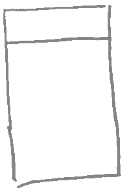
- The seats are very close together, but **you MAY NOT look at your neighbors' exams**. I will be monitoring the classroom for wandering eyes.
- The only materials you may use are pencil, eraser, and calculator.
- Please fill the seats at the end of each row first, otherwise students that arrive later will have to interrupt an entire row to get to a 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 I announce that the exam has ended, **everyone must put down their pencils immediately.** It is not fair if some students stop and others don't. You will hand your exam to the person at the end of your row, and then I will come and pick them up from each row.

1. (30 points) A sample of water is collected from a tidal wetland in San Francisco Bay. After collection the sample bottle contains 450 mL of water and 50 mL of air at 1 atm. The bottle is kept closed while it is transported to the laboratory, and all species reach equilibrium. In the laboratory, the concentration of hydrogen sulfide (H_2S) in the bottle's air is measured and reported to be 88 ppm$_v$. The pH of the water is measured and reported to be 6.8.

   Other useful information:

   H_2S is a di-protic acid with $pK_{a1} = 7.1$, $pK_{a2} = 12.9$
   $K_H (H_2S) = 0.115$ M/atm, at 10°C
   Temp = 10°C

   a. Calculate the total moles of sulfur (S) present in the closed sample bottle (i.e., how many moles of S are present in the air and water?). Round your answer to 3 significant figures.



$P_a = 1$ atm
$V_a = 50$ mL

$V_w = 450$ mL

$$\begin{tikzcd} H_2S_{(g)} \arrow[d, leftrightarrow] & & \\ H_2S_{(aq)} \arrow[r, "7.1"] \arrow[r, phantom, shift right=3ex, "H^+"] & HS^- \arrow[r, "12.9"] \arrow[r, phantom, shift right=3ex, "H^+"] & S^{2-} \end{tikzcd}$$

$$(\text{Moles})_{TOT} = (\text{Moles})_{air} + (\text{Moles})_{H_2S(aq)} + \text{Moles}_{HS^-(aq)} + \underbrace{\text{Moles}_{S^{2-}(aq)}}_{\text{insignificant at pH 6.8}}$$

$(\text{Moles})_{air}$: $P_{H_2S} = Y P_{TOT} = (88\times10^{-6})(1\text{ atm}) = 88\times10^{-6}$ atm

$$n_{air} = \frac{PV}{RT} = \frac{(88\times10^{-6}\text{ atm})(0.05L)\left(\frac{1m3}{10^3L}\right)}{\left(82\times10^{-6}\ \frac{\text{atm}\cdot m^3}{mol\cdot K}\right)(283 K)} = \underline{1.896\times10^{-7}\text{ moles}}$$

$(\text{Moles})_{H_2S(aq)}$: $[H_2S]_{aq} = K_H P_{H_2S} = (0.115\ \frac{M}{atm})(88\times10^{-6}\text{ atm}) = 1.012\times10^{-5}$ M

$$(\text{Moles})_{H_2S(aq)} = [H_2S]V_w = (1.012\times10^{-5}\ \tfrac{mol}{L})(0.45L) = \underline{4.554\times10^{-6}\text{ moles}}$$

$(\text{Moles})_{HS^-}$: $$[HS^-] = \frac{K_{a1}[H_2S]}{[H^+]} = \frac{(10^{-7.1})(1.012\times10^{-5}M)}{(10^{-6.8})} = 5.072\times10^{-6}\text{ M}$$

$$(\text{Moles})_{HS^-} = [HS^-]V_w = \underline{2.282\times10^{-6}\text{ moles}}$$

$$(\text{Moles})_{TOT} = 1.896\times10^{-7} + 4.554\times10^{-6} + 2.282\times10^{-6} = \boxed{7.03\times10^{-6}\text{ moles S}}$$

b. The sample bottle is opened and 100 mg of $FeCl_2$ is added to the water. Will $FeS_{(s)}$ form? Other useful information: K_{sp} (FeS) = 6 x 10^{-19} M^2.

$$K_{sp} = [Fe^{2+}][S^{2-}]$$

$$MW\ FeCl_2 = 55.8 + 2(35.5) = 126.8\ g/mol$$

$$[Fe] = \frac{(0.1\cancel{g})\left(\frac{mol\ FeCl_2}{126.8\ \cancel{g\ FeCl_2}}\right)\left(\frac{1\ mol\ Fe}{1\ mol\ FeCl_2}\right)}{0.45\ L} = 1.7525 \times 10^{-3}\ M$$

$$[S^{2-}] = \frac{K_{a2}[HS^-]}{[H^+]} = \frac{(10^{-12.9})(5.072 \times 10^{-6} M)}{10^{-6.8}} = 4.029 \times 10^{-12} M$$

$$[Fe^{2+}][S^{2-}] = (1.7525 \times 10^{-3} M)(4.029 \times 10^{-12} M) = \underline{7.06 \times 10^{-15} M}$$

$[Fe^{2+}][S^{2-}] > K_{sp}$

$\Rightarrow$ $FeS_{(s)}$ will form

2. (20 points) Mercury is a contaminant in San Francisco Bay, where it accumulates in the sediments. In one part of the bay, the sediments contain 7.24 μg/g mercury and the water in equilibrium with these sediments contains 0.1 ppb (mass fraction) mercury. The sorption of mercury on sediments can be described by a Langmuir isotherm, with $q_{max} = 10$ μg/g. To reduce the mercury concentrations, the most contaminated sediments are dredged. After the system comes to equilibrium again, the remaining sediments are found to contain only 2.2 μg/g mercury. Calculate the concentration of mercury in the water after dredging, assuming it is in equilibrium with the sediments. Round your answer to 3 significant figures.

Initial condition

∇

$C_1 = 0.1\ \mu g/L$

$q_1 = 7.24\ \mu g/g$

Final condition

∇

$C_2 = ?$

$q_2 = 2.2\ \mu g/g$

$q = \frac{bC}{1+bC} q_{max}$ when $q_{max} = 10\ \mu g/g$

b = ? Use initial condition to solve for b

$q_1 + q bC_1 = bC_1 q_{max}$

$bC_{q_{max}} - bC_1 q_1 = q_1$

$bC_1 (q_{max} - q_1) = q_1$

$b = \frac{q_1}{C_1(q_{max} - q_1)}$

$b = \frac{7.24\ \mu g/g}{(0.1\ \frac{\mu g}{L})(10-7.24)\ \frac{\mu g}{g}}$

$b = 26.33\ \frac{L}{\mu g}$

using b, solve for C_2

$C_2 = \frac{q_2}{b(q_{max} - q_2)}$

$= \frac{(2.2\ \mu g/g)}{(26.33\ \frac{L}{\mu g})(10-2.2)\ \frac{\mu g}{g}}$

$\boxed{C_2 = 1.08 \times 10^{-2}\ \mu g/L}$

or 10.8 ppt

3. (25 points) Methane (CH_4) is a potent greenhouse gas. In the atmosphere, it reacts with hydroxyl radical according to the elementary reaction shown below. Answer the questions below, and round your answers to 3 significant figures.

$$CH_4 + OH^{\bullet} \rightarrow CH_3 + H_2O$$

a. The second-order rate constant for the reaction has been reported to be 5.72×10^{-15} cm^3 $molecule^{-1}$ s^{-1} (at 20°C). During the daytime, $[OH^{\bullet}]$ is maintained by photochemical reactions at a constant value of 10^{11} molecules cm^{-3}. Calculate the time it takes for $[CH_4]$ to be reduced by 99% under these conditions.

$$\frac{d[CH_4]}{dt} = -k_2[CH_4][OH^{\cdot}] \sim -k'[CH_4] \quad \text{where} \quad k' = k_2[OH^{\cdot}]$$

pseudo first order rxn

$$\ln\frac{[CH_4]}{[CH_4]_0} = -k't \qquad \frac{[CH_4]}{[CH_4]_0} = 0.01 \quad \text{for 99\% reduction}$$

$$t = -\frac{1}{k'}\ln(0.01)$$

$$k' = \left(5.72\times10^{-15}\ \frac{cm^3}{molecule \cdot s}\right)\left(10^{11}\ \frac{molecule}{cm^3}\right) = \underline{5.72\times10^{-4}\ \frac{1}{s}}$$

$$t = -\frac{1}{5.72\times10^{-4}\ s^{-1}}\ln(0.01)$$

$$\boxed{\begin{aligned} t &= 8050\ s \\ &= 134\ min \\ &= 2.24\ h \end{aligned}}$$

b. In the absence of sunlight, the concentration of $OH^{\bullet}$ will decrease rapidly. If the reaction above is the only relevant reaction (which is a great simplification), what is the characteristic time of $OH^{\bullet}$ under nighttime conditions? Assume that the initial concentration $OH^{\bullet}$ is 10^{11} molecules cm^{-3} and the initial concentration of methane is 10^{15} molecules cm^{-3}.

$$\tau_{char} = \frac{\text{initial conc}}{\text{initial rate}} = \frac{[OH\cdot]}{K_2[CH_4][OH\cdot]} = \frac{1}{K_2[CH_4]}$$

$$= \frac{1}{\left(5.72\times10^{-15}\ \frac{cm^3}{\text{molecule}\cdot s}\right)\left(10^{15}\ \text{molecules}/cm^3\right)}$$

$$\boxed{\tau_{char} = 0.175\ s}$$

4. (25 points) Hydrogen sulfide reacts with manganese oxide according to the reaction below. All species that participate in the reaction are shown <u>except</u> H^+ and OH^-.

$$aMnO_2 + bH_2S \rightarrow cSO_4^{2-} + dMn^{2+} + eH_2O$$

a. What is the oxidation state of Mn in MnO_2?

Mn in MnO_2: $\boxed{+4}$

b. What are the oxidation states of sulfur in H_2S and SO_4^{2-}?

S in H_2S: $\boxed{-2}$

S in SO_4^{2-}: $\boxed{+6}$

c. Balance the redox reaction (determine the values of a, b, c, d, e). You may need to include H^+ or OH^- to balance the reaction. At the end of your solution, please write out the complete, balanced reaction.

e^- balance: Mn: $a(-2) = -2a$ (e^- gained by Mn)

S: $b(+8) = +8b$ (e^- lost by S)

$\Rightarrow 2a = 8b$ let $b = 1$ also $c = b = 1$

$a = 4b$ $a = 4$ $d = a = 4$

Stoichiometry:	LHS	RHS	
Mn	4	4	
S	1	1	
O	8	4+e	$\Rightarrow e = 4$
H	2+?	8	

↑ need 6 H^+ to balance

$$\boxed{4MnO_2 + H_2S + 6H^+ \longrightarrow SO_4^{2-} + 4Mn^{2+} + 4H_2O}$$

Check charge: LHS $+6$ RHS $+8-2=+6$ ✓