CE 111: Environmental Engineering
Midterm Exam #1 (3 October 2012)

Name: SOLUTION

GROUND RULES: This is a closed-book/closed-note exam, except that you are permitted one sheet of notes. Do your work on the paper provided. Please be sure that your name is written on each page you submit. The total score possible is 20 points, and the time allowed is 50 minutes. Use the time wisely. Good luck!

REMINDER: Read the questions carefully, and be certain you are responding appropriately.

HINTS: • If you think you need information that is not given, assume a reasonable value, state your assumption, and proceed. • Partial credit is granted in most places if your work can be understood (and your thinking is reasonable). • All of the information below is true and some of it may be useful.

#1 (2.5 max.) ______ #2 (9 max.) ______ #3 (6 max.) ______ #4 (2.5 max.) ______

Total Score (20 max.): ☐

DATA AND RELATIONSHIPS:

Atomic masses (g/mol):	H = 1, C = 12, N = 14, O = 16
Composition, dry atmos.:	$N_2 = 78\%$, $O_2 = 21\%$, Ar = 1%
Ideal gas law:	$PV = nRT$; $P_iV = n_iRT$
Gas constant:	$R = 0.082$ atm mol^{-1} L K^{-1}
	$R = 82 \times 10^{-6}$ atm mol^{-1} m^3 K^{-1}
Mole fraction:	$y_i = n_i/n = P_i/P$

Conversion factors:

volume:	1 m^3 = 1000 L
volume:	1 L = 1000 cm^3
temperature:	T (K) = T (°C) + 273
distance:	1 ft = 3.28 m
pressure:	1 atm = 101.3 kPa

Pressure in Earth's troposphere: $P(z) = P_o \exp(-z / 7.3\text{km})$

Reaction kinetics for A → products:

0th order $d[A]/dt = -k$

1st order $d[A]/dt = -k[A]$

Definitions: $pH = -\log_{10}([H^+])$ $pK_A = -\log_{10}(K_A)$

Acid-dissociation: $HA \leftrightarrow H^+ + A^-$ $K_A = [H^+][A^-]/[HA]$

Strong acids: H_2SO_4, HSO_4^-, HCl, HNO_3

Weak acids: $H_2CO_3^*$, HCO_3^-, NH_4^+

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1. Pressure Points (2.5 points)

Consider a 2 m^3 container that is initially filled with dry air at P = 1 atm and T = 298 K. If 4.0 moles of dry air are removed and replaced with 4.0 moles of water, what is the equilibrium partial pressure of water vapor in the box (expressed in units of atm) if T = 298 K? Be sure to demonstrate that your answer is correct.

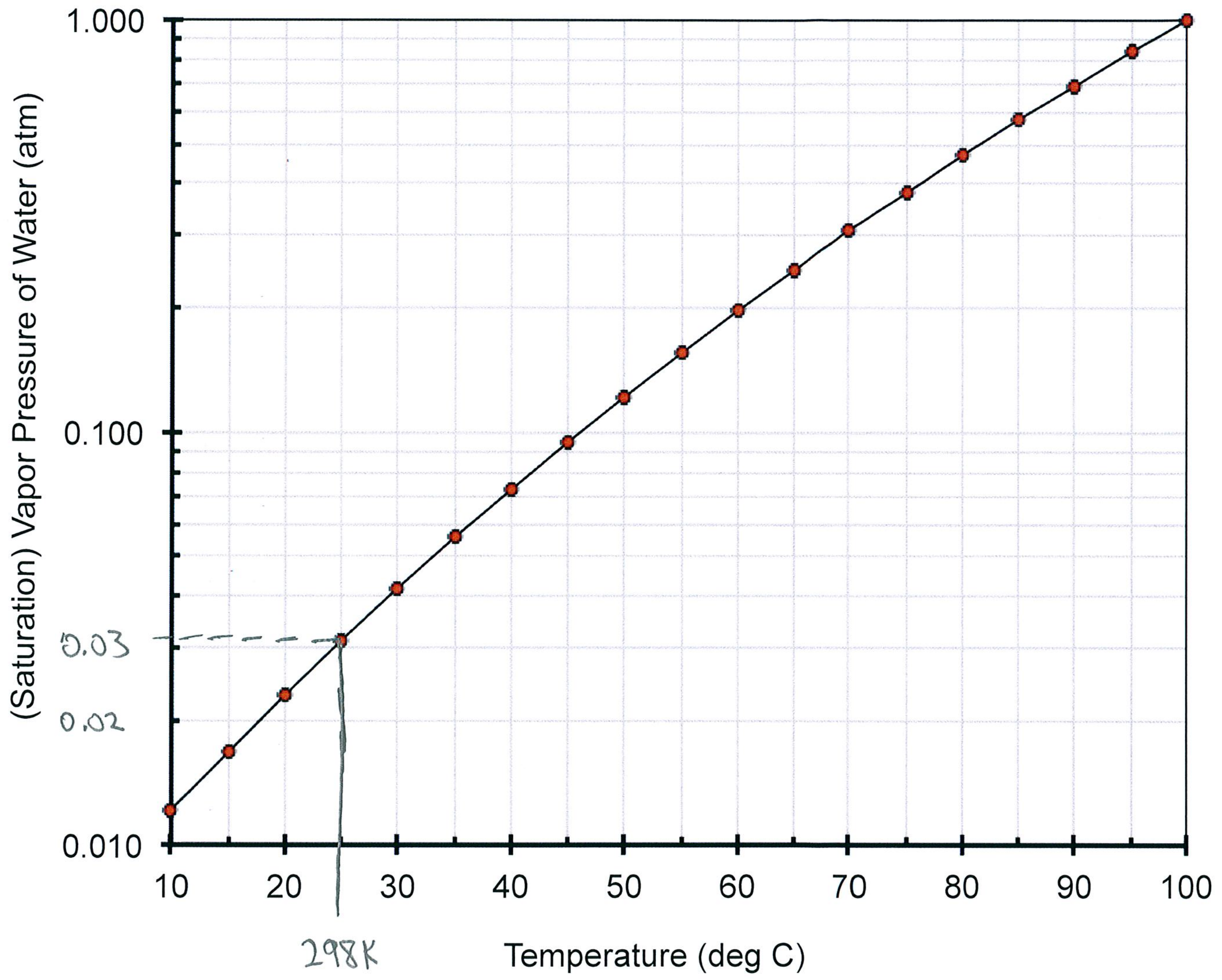

Figure 1. Vapor pressure of water, $P^o_{H_2O}$, versus temperature, T.

If all inserted H_2O remained in gas phase, $P_{H_2O} = \frac{n_{H_2O} RT}{V}$

$$\Rightarrow P_{H_2O} = \frac{4 \text{mol}}{2 \text{m}^3}\left(82 \times 10^{-6} \text{atm m}^3/\text{mol K}\right) 298\text{K} = 0.049 \text{ atm}$$

Compare to equilibrium maximum $P_{H_2O} = P^o_{H_2O} = 0.031$ atm (graph)

$\therefore$ $\boxed{P_{H_2O} = 0.031 \text{ atm}}$ Some H_2O will condense.

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2. Phase Partitioning & Acid-Base Chemistry with Carbonate & Ammonia (9 points)
Consider a raindrop that is in equilibrium with an atmosphere (P = 1 atm) containing carbon dioxide gas, CO_2 (g), at a partial pressure, P_{CO2}, of 3.8 x 10^{-4} atm. CO_2 partitions to the aqueous phase as described by Henry's Law, and participates in acid-base chemistry as shown below.

The raindrop encounters ammonia gas, NH_3 (g), which partitions to the aqueous phase as described by Henry's Law. Ammonia is a base and participates in acid-base chemistry as shown below. The subsequent equilibrium pH of the raindrop is 6.0.

Ammonia partitioning and chemistry:		
Henry's law:	$NH_3\ (g) \leftrightarrow NH_3\ (aq)$	$K_{H,NH3} = 62\ M\ atm^{-1}$
Acid-base reaction:	$NH_4^+ \leftrightarrow NH_3\ (aq) + H^+$	$pK_a = 9.23$
Carbonate partitioning and chemistry:		
Henry's law:	$CO_2\ (g)\ (+ H_2O) \leftrightarrow H_2CO_3^*$	$K_{H,CO2} = 0.034\ M\ atm^{-1}$
Acid-base reaction:	$H_2CO_3^* \leftrightarrow H^+ + HCO_3^-$	$K_{c1} = 4.47 \times 10^{-7}\ M = 10^{-6.35}\ M$
Acid-base reaction:	$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$K_{c2} = 4.68 \times 10^{-11}\ M = 10^{-10.33}\ M$
Dissociation of water:	$H_2O \leftrightarrow H^+ + OH^-$	$K_w = 10^{-14}\ M^2$

(a) Evaluate the following concentration ratios (2 points).

pH = 6 means $[H^+] = 10^{-6}\ M$

$\therefore [OH^-] = 10^{-8}\ M$

$$\frac{[H^+]}{[OH^-]} = \frac{10^{-6}\ M}{10^{-8}\ M} = 100$$

$$\frac{[HCO_3^-]}{[CO_3^{2-}]} = \frac{[H^+]}{K_{c2}} = \frac{10^{-6}\ M}{10^{-10.33}\ M} = 10^{4.33}$$

(b) What is the partial pressure of ammonia, P_{NH3}? (7 points)

$[NH_3] = K_{H,NH_3} P_{NH_3}$

① $\boxed{P_{NH_3} = [NH_3]/K_{H,NH_3}}$

How to determine $[NH_4^+]$?

(Next page)

From Ka, $\boxed{[NH_3] = Ka[NH_4^+]/[H^+]}$ ②

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EN: $[H^+] + [NH_4^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

Can evaluate H^+, OH^-, HCO_3^- and CO_3^{2-}, but from part (a) we know we can drop OH^- and CO_3^{2-}

$$\therefore \boxed{[NH_4^+] = [HCO_3^-] - [H^+] = [HCO_3^-] - 10^{-6}\,M} \quad ③$$

From K_{c1}, $\boxed{[HCO_3^-] = K_{c1}[H_2CO_3^*] / [H^+]}$ ④

From K_{H,CO_2} $\boxed{[H_2CO_3^*] = K_{H,CO_2}\, P_{CO_2}}$ ⑤

Solve: $[H_2CO_3^*] = (0.034\,\frac{M}{atm})(3.8 \times 10^{-4}\,atm) = 1.29 \times 10^{-5}\,M$

$$[HCO_3^-] = \frac{10^{-6.35}\,M}{10^{-6}\,M}(1.29 \times 10^{-5}\,M) = 5.76 \times 10^{-6}\,M$$

$$[NH_4^+] = 5.76 \times 10^{-6}\,M - 10^{-6}\,M = 4.76 \times 10^{-6}\,M$$

$$[NH_3] = \frac{10^{-9.23}}{10^{-6}}(4.76 \times 10^{-6})\,M = 2.80 \times 10^{-9}\,M$$

$$P_{NH_3} = 2.80 \times 10^{-9}\,M / 62\,M/atm$$

$\boxed{P_{NH_3} = 4.5 \times 10^{-11}\,atm}$ $\quad Y_{NH_3} = 45\,ppt$

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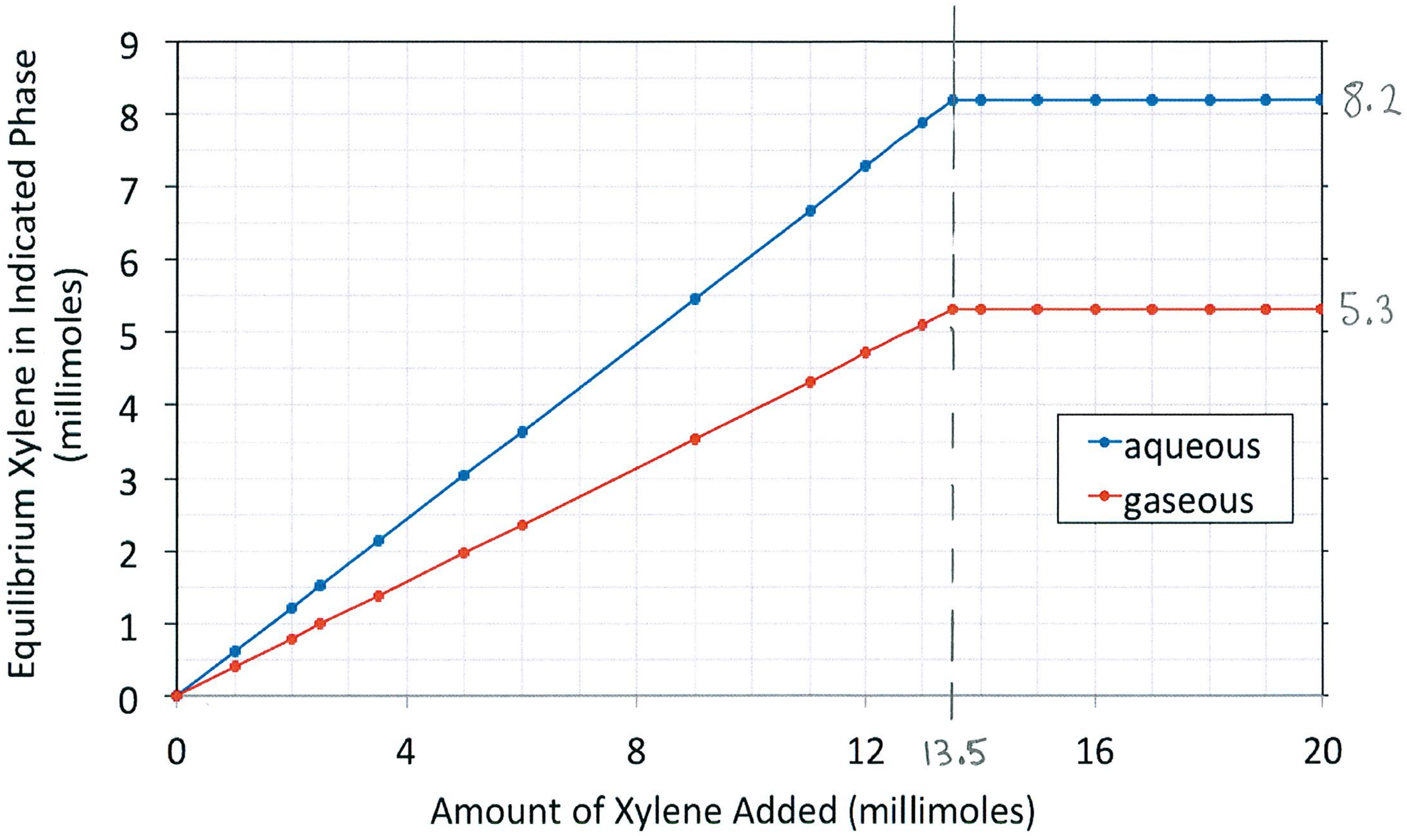
3. Phase Partitioning with Sorption (6 points)

Consider the following experiment. A closed vessel contains $V_w = 5$ L of liquid water and $V_g = 20$ L of gas space. A known number of moles of xylene (C_8H_{10}, MW = 106 g/mol) are added to the vessel. At equilibrium, the moles of gaseous xylene and aqueous xylene are separately determined and plotted on the graph below. This is repeated several times with increasing amounts of xylene. The experiment stops after 20 millimoles of xylene have been added. The temperature is maintained constant at 298 K during the experiment. Refer to the results of the experiment shown below as needed to answer questions 3a and 3b on this page and the next page.



(a) What is the water solubility of xylene? Express your answer in mg/L units (1 point).

$$C_{sat} = \frac{8.2\ \text{mmol}}{5\ \text{L}}\left(\frac{106\ \text{g}}{\text{mol}}\right) = \boxed{174\ \text{mg/L}}$$

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(b) After the 20 millimoles have been added, activated carbon is added to this system. The activated carbon sorbs xylene as described by the Freundlich isotherm:

$q_e = K_f\,C_e^{1/n}$ where q_e and C_e are expressed in units of mg/g and mg/L, respectively,

$K_f = 85$ mg/g (L/mg)$^{1/n}$ and $1/n = 0.16$

What is the *minimum* amount of activated carbon (in grams) that must be added to ensure that, when all phases of xylene are in equilibrium, the system does not contain any NAPL of xylene (5 points)?

$$\underset{\substack{\uparrow \\ 20\,\text{mmol}}}{n_{total}} = \underbrace{n_{aq} + n_{gas}}_{\substack{13.5\,\text{mmol} \\ \text{(from graph)}}} + n_{sorbed} + \underset{\substack{\swarrow \\ \emptyset}}{\cancel{n_{NAPL}}}$$

$\therefore\ n_{sorbed} = 6.5\,\text{mmol}$

$$\boxed{q = \frac{\text{mg sorbed}}{\text{g AC}} = 85\,C_e^{0.16}}$$

$\Rightarrow$ mg sorbed $= 6.5\,\text{mmol}\,(106\,\text{g/mol}) = 689$ mg sorbed

$\Rightarrow$ from part (a), $C_e = 174$ mg/L

$$\therefore\ g\,AC = \frac{689\,\text{mg}}{(85)\,174^{0.16}\,\frac{\text{mg}}{\text{g}}} = \frac{689}{194}\,g$$

$$\boxed{g\,AC = 3.6\,g}$$

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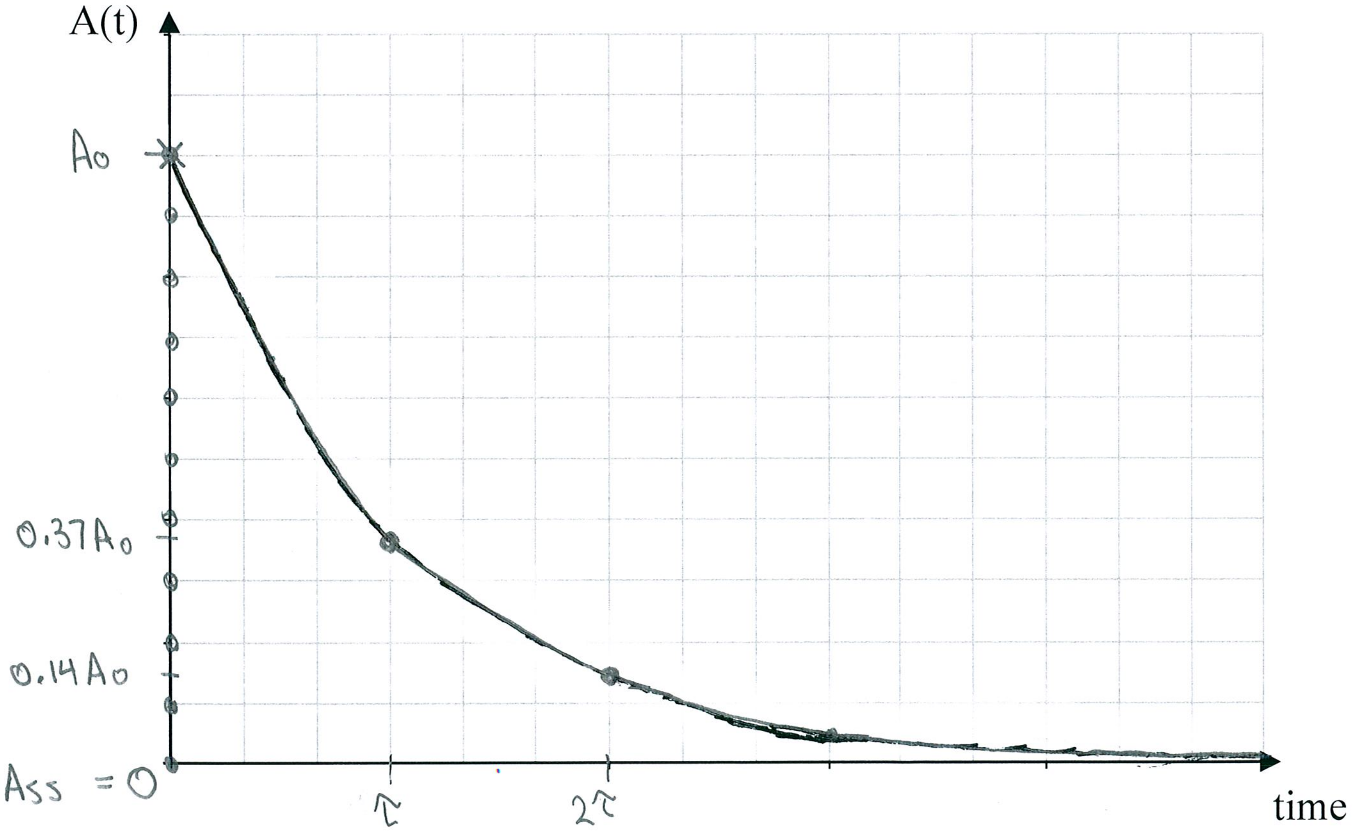
4. Kinetics (2.5 points)

Consider the following chemical reaction. The rate of the reaction is first order in A with rate constant k. At t = 0, the initial concentrations of A and B are A(t=0) = A_o and B(t=0) = 0.

$$A \xrightarrow{k} 0.5B$$

On the following graph, sketch the time varying concentration of **A(t).** To ensure that you show the correct shape and receive full credit, indicate: (i) the initial concentration, A_o, (ii) the value of the reaction characteristic time, τ, and *in terms of A_o* (iii) the concentration evaluated at τ, A(t=τ), (iv) the concentration evaluated at 2τ, A(t=2τ), and (v) the ultimate steady state concentration, A_{ss}, when dA/dt = 0.



1st order means $\frac{dA}{dt} = -kA$, $\tau \sim \frac{\text{Stock}}{\text{flow}} = \frac{A_o}{kA_o} = \frac{1}{k}$

$A(t) = A_o \exp(-kt)$

t	A(t)
0	A_o
τ	$0.37A_o$
2τ	$(0.37)\,0.37A_o = 0.14A_o$
>> τ	~0

$\frac{dA}{dt} = 0$ when rxn stops
when A = 0

∴ $A_{ss} = 0$