CHM 5423 – Atmospheric Chemistry
Problem Set 4 - Due date: Sunday, March 28th (by 11:59pm). Please turn in your homework by sending it to me at my FIU email address joensj@fiu.edu Indicate in your email that you are sending me your Homework 4 solutions.

Do the following problems. Show your work.

1) The major initial daytime reaction for the removal of alkenes from the troposphere is reaction with OH radical

$$\text{alkene} + OH \rightarrow \text{“products”} \qquad (1.1)$$

The following rate constants are experimental values for reaction 1.1 at p = 1.00 atm and T = 298. K.

compound	k (cm^3/molecule•s)	compound	k (cm^3/molecule•s)
ethene	8.52×10^{-12}	1-pentene	31.4×10^{-12}
propene	26.3×10^{-12}	1-hexene	$37. \times 10^{-12}$
1-butene	31.4×10^{-12}	1-heptene	$40. \times 10^{-12}$

For data such as this, where the reacting organic molecules follow a simple trend (in this case, becoming larger by the addition of a CH_2 group as we move down the list) it might be expected that the data can be fit to a simple equation for predicting the numerical value for the rate constant.

a) Before find an equation to model the above data, should you exclude the rate constant for the ethene + OH reaction? Why or why not?

b) Before find an equation to model the above data, should you exclude the rate constant for the propene + OH reaction? Why or why not?

c) Find an expression for predicting the rate constant for reaction 1.1

d) Based on your answer in c, are there any “suspicious” rate constants in the data table? Explain your answer.

2) The reaction of n-propyl alcohol ($CH_3CH_2CH_2OH$) with hydroxyl radical

$$CH_3CH_2CH_2OH + OH \rightarrow \text{“products”} \qquad (2.1)$$

has several possible initial products.

a) What are the possible initial products expected for reaction 2.1? Which do you expect to be the most likely initial product to form? Why?

b) For each possible initial product for reaction 2.1, give the first stable product expected to form (you do not need to give any of the intermediate reactions).

c) What other processes, if any, would you expect to be important in the removal of n-propyl alcohol from the troposphere? Why?

3) The peroxyacteyl nitrate compound PnBN, $CH_3CH_2CH_2C(O)OONO_2$, thermally decomposes in the atmosphere

$$CH_3CH_2CH_2C(O)OONO_2 \rightarrow CH_3CH_2CH_2C(O)OO + NO_2 \qquad (3.1)$$

The rate constant for the therml decomposition of PnBN is

$$k = (3.2 \times 10^{18}\ s^{-1}) \exp[(-15100.\ K)/T] \qquad (3.2)$$

a) What is E_a, the activation energy, for reaction 3.1 Give your final answer in units of kJ/mol.

b) Reaction 3.1 is an example of a unimolecular gas phase reaction. Would you expect the reaction to be unimolecular in the limit $p \rightarrow 0$? Why or why not?

c) Find the numerical value for reaction 3.1 and the corresponding half-life for the reaction at T = 288. K and T = 250. K. Give your final answer in an appropriate set of units (s/min/hr/day/year, depending on the value of the half-life).

d) PnBN forms from the recombination reaction with NO_2

$$CH_3CH_2CH_2C(O)OO + NO_2 + M \rightarrow CH_3CH_2CH_2C(O)OONO_2 + M \qquad (3.3)$$

Therefore the combination of reactions 3.3 and 3.1 have no effect on the concentration of NO_2 in the troposphere. Despite this, the reactions are considered important in tropospheric chemistry, particularly for the chemistry of remote regions (those far away from urban areas or other soures of NO_x). Explain this observation.

4) The Leighton mechanism is a relationship among the concentrations of NO, NO_2, and O_3 in the troposphere during the daytime. The basic mechanism has three steps:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (4.1)$$

$$NO_2 + hc/\lambda \quad NO + O(^3P) \qquad (4.2)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (4.3)$$

As discussed in class, use of the steady state approximation leads to the following relationship:

$$\frac{[NO]}{[NO_2]} = \frac{J_2}{k_1 [O_3]} \qquad (4.4)$$

Experimentally, the value for the rate constant k_1 is

$$k_1 = (3.0 \times 10^{-12}\ cm^3/molecule \cdot s) \exp[-(1500\ K)/T] \qquad (4.5)$$

a) Find the numerical value for k_1 at T = 285. K, 260, K, and 235. K

b) For T = 285. K and $[O_3] = 2.6 \times 10^{12}$ molecule/cm^3, the following are observed in the lower troposphere

$$[NO_x] = [NO] + [NO_2] = 1.0 \times 10^{12}\ molecule/cm^3 \qquad (4.6)$$

$$[NO]/[NO_2] = 0.22 \qquad (4.7)$$

Based on this find [NO] and $[NO_2]$. Give your final answers in units of molecules/cm^3. Also find the numerical value for J_2, including correct units, and $t_{1/2}$ for NO_2 with respect to photodissociation. Explain why the value for half-life for NO_2 found here is misleading in terms of how much NO_2 is present in the troposphere.

c) NO_2 can be permanently removed from the troposphere by the reaction

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad (4.8)$$

The effective bimolecular rate constant for reaction 4.8 for the conditions in this problem is $k = 1.1 \times 10^{-11}$ cm^3/molecule•s. Use this result to find $t_{1/2}$ for NO_x. Assume $[OH] = 1.0 \times 10^6$ molecule/cm^3. Is this a better value for the half-life of NO_2 in the troposphere than the value found in part b of this problem? Why or why not?