CHM 5423 – Atmospheric Chemistry
Problem Set 3 - Due date: Thursday, March 18th (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 3 solutions.

NOTE: Exam 2 will be a take home exam. I will pass out the exam on Tuesday, March 30th. Note this is a change from the original date given in the syllabus.

Do the following problems. Show your work.

1) There are some molecules (for example, PANs) whose removal in the troposphere is by an apparent first order (unimolecular) reaction.
    Consider the following general model for a unimolecular decomposition reaction:

    step 1 $AB + M \rightleftarrows AB^* + M$ (1.1)

    step 2 $AB^* \rightarrow A + B$ (1.2)

In the above mechanism AB* is an energized molecule (a molecule with sufficient energy to decompose), and M represents any gas phase molecule.
    a) Find a general expression for d[A]/dt, the rate of the decomposition reaction. Note that your final expression cannot be in terms of AB*, which is a reaction intermediate.
    b) Use your result from a to find the value for the apparent rate constant for the reaction in the low pressure ([M] $\rightarrow$ 0) and high pressure ([M] $\rightarrow$ ∞) limits.
    c) What would a plot of k_{uni} (the unimolecular rate constant) vs [M] look like? Which regions in the plot would correspond to the low pressure, falloff, and high pressure regions.
    d) For some decomposition reactions it is not possible to find the high pressure limiting rate constant. Suggest a reason for this.

2) The following questions concern the paper by Crawford et al. "Kinetic of OH radical reaction…" which is posted on the class web page.
    a) Why was helium used as a carrier gas in the generation of hydroxyl radicals? What other gases do you think could also have been used, and why?
    b) Water vapor was added to the system <u>after</u> the generation of fluorine atoms by a microwave discharge, and was not included in the F$_2$/helium mix. Why was this done?
    c) What is $\Delta H°_{rxn}$ for the process

    $F + H_2O \rightarrow HF + OH$

Why is this an important factor to consider (hint – think about generating hydroxy radicals by a microwave discharge through Cl$_2$).
    d) What is the advantage of using two compounds (in this case n-octane and n-nonane) as reference compounds in the relative rate measurement for the n-heptane + OH reaction?
    e) Figure 4 of the paper gives a plot of ln(k) vs (1/T) for the n-hexane + OH reaction. Is there any evidence for non-Arrhenius behavior over the temperature range of the plot? Justify your answer.
    f) Would the method used in this study be appropriate to use in a study of the alkene + OH addition reaction? Why or why not?

3) The recommended value for the rate constant for the reaction

$$OH + CH_4 \rightarrow H_2O + CH_3 \tag{3.1}$$

is

$$k = A\ T^n \exp(-B/T) \tag{3.2}$$

$$A = 1\ 85 \times 10^{-20}\ cm^3/molecule \cdot s \qquad n = 2.82 \qquad B = 987\ K$$

      a) Using eq 3.2, calculate the value for k for reaction 3.1 at T = 200, 220, 240, 260, 280, and 300 K.
      b) Using your results in part a, plot of ln(k) vs 1/T (I would suggest you use EXCEL to do this). Based on the results, find the values for A and E_a (pre-exponential factor and activation energy) assuming that the Arrhenius equation applies to reaction 3.1 over the temperature range 200 K – 300 K..
      c) Using the values for A and E_a found in part b, recalculate the value for k at the same temperatures as in part a of the problem.
      d) At each temperature find the percent difference between the value for k found using eq 3.2 and the value using the Arrhenius equation.

$$\text{\% difference} = \frac{|k_{3.2} - k_{Arr}|}{k_{3.2}} \times 100\ \% \tag{3.3}$$

where $k_{3.2}$ is the value of k found using eq 3.2 and k_{Arr} is the value using the Arrhenius equation.
      e) Assuming that the values for k found from eq 3.2 are correct, what is the maximum error that is introduced by using the Arrehenius equation to model the temperature dependence for k over the range of temperatures found in the troposphere? Do you think this is a significant amount of error? Why or why not?
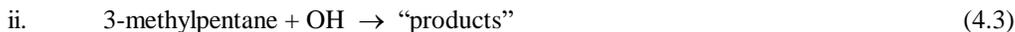
4) In class we discussed a method for estimating the rate constant and branching ratio for the alkane + OH reaction. In the most simple model the rate constant is given by the following expression:

$$k = N_p\ k_p + N_s\ k_s + N_t\ k_t \tag{4.1}$$

where N_p, N_s, and N_t are the total number of primary, secondary, and tertiary hydrogens in the alkane, and k_p, k_s, and k_t are rate constants for the abstraction of primary, secondary, and tertiary hydrogens. In this problem we will use the following values for these rate constants (which assume T = 298. K).

$$k_p = 0.45 \times 10^{-13}\ cm^3/molecule \cdot s \qquad k_s = 4.7 \times 10^{-13}\ cm^3/molecule \cdot s \qquad k_t = 19.5 \times 10^{-13}\ cm^3/molecule \cdot s$$

      Consider the following two alkane + OH reactions at 298. K

    i.   propane + OH $\rightarrow$ "products"   (4.2)

    ii.   3-methylpentane + OH $\rightarrow$ "products"   (4.3)

Find the following for reaction i. and ii.
      a) k, the overall rate constant for the reaction at T = 298. K.
      b) All of the possible initial products of the alkane + OH reaction, and the branching ratio (fraction of the total reaction) forming each initial product
      c) For propane, also give the entire sequence of reactions that take place in the troposphere, starting with reaction i. and ending when a stable product is formed.
      d) Experimentally, it is far easier to measure the overall rate constant for the alkane + OH reaction than it is to find the branching ratios for the initial products of the reaction. Why do you think this is true?