CHM 5423 – Atmospheric Chemistry
Problem Set 3
Due date: Tuesday, February 19th. The first hour exam is on Thursday, February 21st. It will cover material from the first four handouts for the class.

Do the following problems. Show your work.

1) The chemical reaction

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (1.1)$$

plays an important role in ozone destruction. Because of this, it has been extensively studied both experimentally and theoretically.

The Arrhenius constants for the reaction are $A = 2.3 \times 10^{-11}$ cm^3/molecule•s and $E_a = 1.67$ kJ/mol. Based on this information find the value for k for reaction 1.1 at T = 250. K and T = 300. K.

2) Baasandorj and coworkers (J.Phys.Chem.A 114 (2010) 4619-4633) studied the gas phase reaction of hydroxyl radical (OH) with CH_2=CHF. A summary of their data is given below

T(K)	220.	249.	296.	321.	373.
k(cm^3/molecule•s)	7.37×10^{-12}	6.31×10^{-12}	5.18×10^{-12}	4.92×10^{-12}	4.06×10^{-12}

a) Fit the above data to the Arrhenius equation. Find the values for A and E_a corresponding to the data.

b) If you have done the fitting correctly you will have obtained a negative value for E_a, which is difficult to reconcile with a direct reaction. Consider the following mechanism for the reaction

step 1 $\quad OH + CH_2{=}CHF \leftrightarrows (OH\text{-}CH_2{=}CHF) \qquad k_1, k_{-1} \qquad (2.1)$

step 2 $\quad (OH\text{-}CH_2{=}CHF) + M \rightarrow$ "product" $\qquad k_2 \qquad (2.2)$

Find a general expression for the rate law predicted for the above mechanism.

c) Your general expression in b has the following low pressure ([M] $\rightarrow$ 0) limiting behavior

$$d[product]/dt = (k_1k_2/k_{-1}) [OH][CH_2{=}CHF] \qquad (2.3)$$

Assume that k_1, k_{-1}, and k_2 each obey the Arrhenius equation. For what conditions, if any, will the observed rate law for the reaction have a negative activation energy?

3) The general solution for second order heterogeneous kinetics for a reaction with stoichiometry and rate law

$$A + B \rightarrow \text{"products"} \qquad d[A]/dt = - k [A] [B] \qquad (3.1)$$

is, as discussed in class

$$kt = \frac{1}{([B]_0 - [A]_0)} \ln \frac{[A]_0 [B]_t}{[B]_0 [A]_t} \qquad [B]_0 \neq [A]_0 \qquad (3.2)$$

Show that in the limit $[B]_0/[A]_0 \rightarrow \infty$ eq 3.2 takes on the same form as the solution for a first order chemical reaction

$$[A]_t = [A]_0 \exp(- k_{obsd}t) \qquad (3.3)$$

and find an expression for k_{obsd}, the apparent first order rate constant.

4) The following question concerns the paper "Rate constant for the reaction of OH with H_2 between 200 and 480 K" by V. L. Orkin and coworkers (**J.Phys.Chem.A** (2006) **110**, 6978-6985). A copy of the paper is available at my website. Note that to answer some of the questions you may have to go to additional sources for information or perform calculations.

a) On page 6978 of the paper the main source of molecular hydrogen in the Earth's atmosphere is identified as photodissociation of formaldehyde

$$HCHO + hc/\lambda \rightarrow CO + H_2 \qquad (4.1)$$

If photodissociation occurs at λ = 350. nm, how much excess energy will be available for the photodissociation products? Where will that energy go? What will happen to the excess energy over time?

$\Delta H°_f(CO)$ = - 110.53 kJ/mol $\Delta H°_f(HCHO)$ = - 108.57 kJ/mol $\Delta H°_f(H_2)$ = 0.0 kJ/mol

b) The technique used in the experiments reported in the paper was flash photolysis. Briefly describe this technique. How was flash photolysis used to produce hydroxyl radicals in the experiment?

c) The method used to monitor OH radial concentration in the experiments was resonance fluorescence. Briefly describe this technique. How was this method applied in this paper to detect OH radicals?

d) The data obtained in this experiment was corrected for the effect of OH diffusion. What does this mean? Why is this an important correction? How was the correction carried out?

e) Use eq 15 on page 6983 to find the value for k for the reaction of H_2 with OH at T = 272. K, the estimated average temperature of the troposphere.

f) The authors report an estimated lifetime for H_2 of 10 years (note – remember the difference between lifetime and half-life for a chemical reaction). Assuming an average tropospheric temperature T = 272 K, and assuming that reaction of H_2 with OH is the only important process removing molecular hydrogen from the atmosphere, what is the value for [OH], the average value for the hydroxyl radical concentration in the troposphere? Give your answer in units of molecules/cm^3.