AOSC 433/633 & CHEM 433/633 Atmospheric Chemistry and Climate

Problem Set #3 (220 Points)

Due: March 28, 2013 (at start of class)

Late penalty: *15 points* per day late, unless there is a legitimate medical or extra-curricular circumstance (i.e., band, athletics, GREs, etc) brought to our attention **prior to the due date!**

Final deadline: Monday, 1 April, 6 pm: **no credit** will be given after final deadline.

Please show all work!

1. Lifetimes with respect to Photolysis and Reaction w/ OH (100 Points)

The Montreal Protocol has banned the industrial production of halon-1301 (CF_3Br), which had been used to extinguish fires. N-propyl bromide (C_3H_7Br or $CH_2BrCH_2CH_3$) is a solvent that has been proposed as a suitable replacement CFC-113 ($C_2Cl_3F_3$ or CCl_2FCClF_2). CFC-113 has also been banned by the Montreal Protocol whereas n-propyl bromide is not presently regulated:

http://ozone.unep.org/new_site/en/Treaties/decisions_text.php?dec_id=930

Bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2) are natural compounds produced by algae in the biologically productive tropical oceans. These gases and are also not regulated, as they do not have significant industrial sources. We will examine the loss frequencies of these compounds near the surface and in the stratosphere and will then consider public if the public policy is reasonable.

a) (30 points) Much scientific interest resides in establishing where in the atmosphere a particular compound is lost. Here we will compute the J value (photolysis frequency) for each of these species at 0 km altitude (the surface) and 40 km altitude (the stratosphere), using values of solar actinic flux given in Table A and absorption cross sections given in Table B. Please pay attention to the units of these numbers! Files with numerical values of the information in these tables can be found at (txt files):

www.atmos.umd.edu/~rjs/class/spr2013/problem_sets/TableA.txt

www.atmos.umd.edu/~rjs/class/spr2013/problem_sets/TableB.txt

or (same info in excel format):

www.atmos.umd.edu/~rjs/class/spr2013/problem_sets/TableA.xls

www.atmos.umd.edu/~rjs/class/spr2013/problem_sets/TableB.xls

Values for solar actinic flux are from Chapter 3 of *Chemistry of the Upper and Lower Atmosphere* by Finlayson-Pitts and Pitts, for a solar zenith angle (SZA) of 40°, which provides a good representation of daytime conditions.

Assume in all cases the absorption is fully dissociative: i.e., quantum yield = 1 at all wavelengths.

Also, in class (i.e., Slide 3, Lecture 10) the units of solar actinic flux were given as photons cm^{-2} s^{-1} nm^{-1} whereas the table from Finlayson-Pitts and Pitts uses units of photons cm^{-2} s^{-1} for this same quantity, which applies for the specified wavelength intervals. Please try to use this information to deduce how the Δ(Wavelength) needed to evaluate the interval has been accommodated, and as always, contact an instructor if you have any questions.

Compute the J value (photolysis frequency) for the four species at the two altitudes and enter the results in the table below. Please show your work, and also indicate the units of the J values ☺

	0 km	40 km
J_{CF3Br}		
$J_{CH2BrCH2CH3}$		
J_{CHBr3}		
J_{CH2Br2}		

Notes:

1. **You may carry out the calculations in EXCEL or any programming language. Please show your work and indicate how the J values have been found.**
2. **For one entry, the value is the result of a "trivial" calculation you could carry out in your head (really!). We are asking you to conduct this calculation to emphasize the fact that the J value is the product of the cross section and the solar actinic flux.**

b) (20 points) Assuming a temperature of 272 K and a value of 1×10^6 molecules cm^{-3} for global mean tropospheric [OH], find the lifetime for removal of CF_3Br, $CH_2BrCH_2CH_3$, $CHBr_3$, and CH_2Br_2 by reaction with OH in the troposphere. Express the result in units of *days*, and write the final values in the appropriate column of the table below.

To complete this question, you will need to use the table of bimolecular rate constants:

http://www.atmos.umd.edu/~rjs/class/spr2013/supplemental_readings/JPL2010_Bimolecular_Rates.pdf

	Photolysis, 0 km	Reaction OH, 0 km	Photolysis, 40 km
τ_{CF3Br}			
$\tau_{CH2BrCH2CH3}$			
τ_{CHBr3}			
τ_{CH2Br2}			

c) (10 points) The numerical value for the lifetime for removal of CF_3Br by reaction with OH actually represents a lower limit to the actual value. Why is this value a lower limit?

d) (10 points) Compute the lifetime for loss of the four species, with respect to photolysis, at 0 and 40 km altitude, in units of days, and place the resulting values in the appropriate column of the table that appears on page 2.

   Hint: It is rather simple to compute lifetime (units of time) from photolysis frequency (units of inverse time)

e) (30 points) Based on the values of the lifetimes for loss by photolysis at the surface, for loss by reaction with tropospheric OH, and loss by photolysis in the stratosphere:

   1) Which compound will decompose most rapidly in the troposphere due to reaction with OH?

   2) Which compound will decompose most rapidly in near the surface due to photolysis?

   3) Which compound could possibly cross the tropopause, intact, depending on the rapidity of convection?

   4) Which compound will almost certainly be lost only in the stratosphere?

   5) Based on your calculations, was the Montreal Protocol wise to have banned the production of Halon-1301?

   6) Based on your calculations, should society be concerned about damage to the ozone layer caused by increased future production of n-propyl bromide?

2. (120 points) Production of Tropospheric Ozone. Here, we will evaluate the dependence of the production of tropospheric ozone on the abundance of NO, which is central to tropospheric chemistry.

Our calculation will be conducted at the surface, for a hot summer day with a temperature of 96 degrees Fahrenheit and an atmospheric density [M] of 2.5×10^{19} molecules cm^{-3}.

The production of tropospheric ozone is limited by the reaction of HO_2+NO; hence, we write:

$$\text{Prod Ozone} = k_{HO2+NO} \, [HO_2] \, [NO] \tag{1}$$

The loss of HO_x is equal to:

$$\text{Loss of } HO_x = 2 \, k_{HO2+HO2} \, [HO_2]^2 + k_{OH+NO2+M} \, [M] \, [OH] \, [NO_2] \tag{2}$$

Assume that the production rate of HO_x due to the reaction $O(^1D)+H_2O$ occurs at a rate of 0.75 ppt s^{-1} (parts per trillion per second) and also that production of HO_x is balanced by loss of HO_x, which is given by the above expression.

The ratio of [OH] to $[HO_2]$ is controlled by two reactions: OH+CO which causes loss of OH and HO_2+NO which reforms OH. Hence, a balance of production and loss for OH leads to:

$$k_{CO+OH} \, [CO] \, [OH] = k_{HO2+NO} \, [HO_2] \, [NO] \tag{3}$$

We will represent the entire mix of VOCs in the atmosphere as CO, which we will assume has a mixing ratio of 3200 ppb (this is a simplified treatment for a highly polluted atmosphere). Finally, assume the ratio $[NO_2]/[NO] = 10$ at all times (this final equality allows us to solve the problem using pencil and paper, rather than a computer code ☺).

By substituting (3) into (2), we can show:

$$\text{Prod of } HO_x = 2 \, k_{HO2+HO2} \, [HO_2]^2 + R \, [HO_2] \, [NO]^2 \tag{4}$$

a) (20 points) What is the symbolic value of R in equation (4) (i.e., what combination of rate constants and other parameters does R represent)?

b) (20 points) What is the numerical value of R ?

Note: rates for all reactions should be obtained from the table of bimolecular rates constants posted at:

   http://www.atmos.umd.edu/~rjs/class/spr2013/problem_sets/JPL2010_Bimolecular_Rates.pdf

except for:

   the rate constant of the three body reaction $OH+NO_2+M$, which has a value of 4.8×10^{-31} cm^6 sec^{-1}

   the rate constant for $OH+CO$, which has a value of 2.4×10^{-13} cm^3 sec^{-1} for our conditions.

      We've provided numerical values for both of these rate constants because the expressions are more
      complicated to evaluate than those used for standard bimolecular reactions.

c) (20 points) Use expression (4) to find [HO$_2$], in units of molecules/cm^3, for the following values of [NO]:
      10, 650, 1000, 2500, and 5000 ppt (parts per trillion)
      Note: you must first convert [NO] to molecules cm^{-3}.

d) (20 points) Evaluate expression (1), the production rate of tropospheric ozone, for each value of [NO] given in part C. Express the answer in units of molecules cm^{-3} s^{-1}.

f) (20 points) Sketch, or use a program to plot, the production rate of tropospheric ozone as a function of [NO].

g) (20 points) Explain why the production rate of ozone varies in such a non-linear manner as a function of the value of [NO] _and_ state why knowledge of where the troposphere lies, on the curve drawn in part f), is so important for air quality regulation.

3. Graduate Students Only (50 points)

This question is assigned **_only to the students_** enrolled in AOSC 633 or CHEM 633. If undergraduate students would like to work through the problem, they are welcome to do so. *But no extra credit will be given to undergraduates for solving this problem* **!** Sorry but if we were to give extra credit then the problem would no longer be exclusively assigned to graduate students ☺

i) (10 points) Produce a plot of the production rate of ozone, using **units of ppb hour^{-1}**, for the following values of the HO$_x$ production rate: 0.1 ppt s^{-1}, 0.75 ppt s^{-1}(value used above) and 1.2 ppt s^{-1}. Note: results above were found, presumably, in units of molecules cm^{-3} s^{-1}, so you will need to convert to ppb hour^{-1}.

ii) (10 points) Determine the value of NO where each of these three curves reaches a maximum.

iii) (10 points) Explain why the maximum value of the production curve varies with NO in the manner determined above.

iv) (20 points) Scientists at the University of California, San Diego reported that the reaction of electronically excited NO$_2$ with H$_2$O may provide an important source of HO$_x$ (*Li et al., Science, 319, 1657, 21 March 2008*) that until their study had been overlooked in models of atmospheric composition. In a commentary that accompanied this article (*Wennberg and Dabdub, Science, 319, 1624, 21 March 2008*), Drs. Wennberg and Dabdub showed that this new source of HO$_x$ leads to a considerable increase in the amount of tropospheric O$_3$ at the surface in Southern California, as illustrated below:
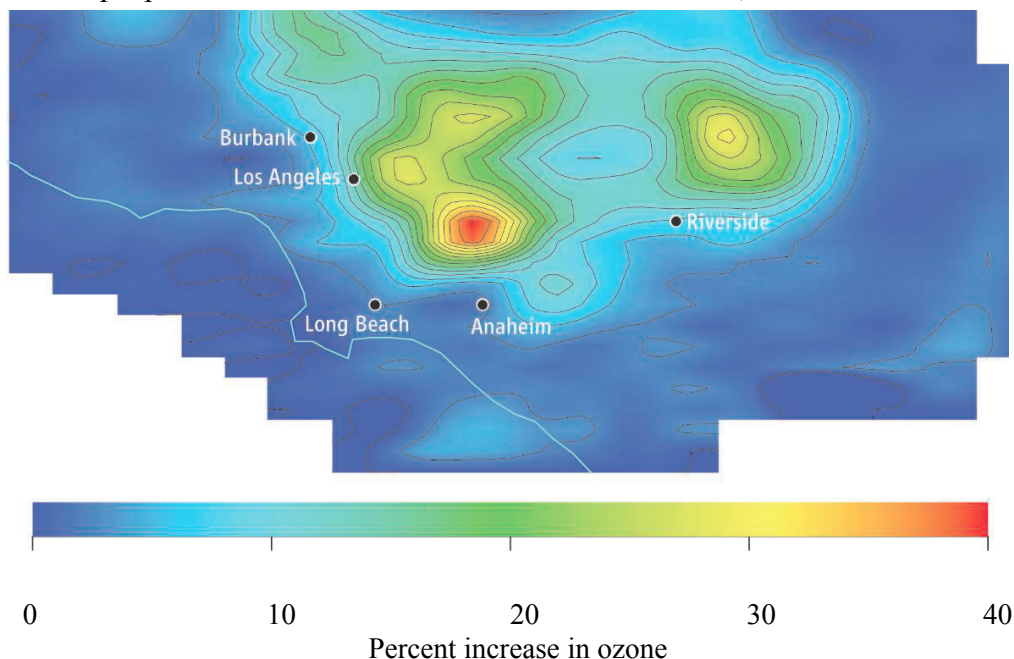
More pollution? The difference between photochemical simulations for 27 to 29 August 1987 in California obtained with and without including the OH source from the reaction of electronically excited NO$_2$ with H$_2$O described by Li et al. (2008). The figure shows the percentage increases in O$_3$ due to this new chemical process.

Explain why Drs. Wennberg and Dabdub found that this new source of HO$_x$ leads to a considerable increase in modeled surface ozone.