ATMS/CHEM 458 Problem Set 3 Due in class: Wednesday Nov 10 2010

In this problem set you will analyze observations of radical species made during the SPADE (Stratospheric Photochemistry, Aerosols and Dynamics Expedition) aircraft measurement campaign on May 11 and May 12 1993. This mission used NASA's ER-2 aircraft with measurements of OH, HO_2, ClO, NO, NO_2, O_3, and radiation field.

Here are some reactions and their mean rate constants that you will use:

R1	$OH + O_3$	$\rightarrow HO_2 + O_2$	$k_1 = 2 \times 10^{-14}$ cm^3 molec^{-1} s^{-1}
R2	$HO_2 + O_3$	$\rightarrow OH + 2O_2$	$k_2 = 1 \times 10^{-15}$ cm^3 molec^{-1} s^{-1}
R3	$HO_2 + NO$	$\rightarrow OH + NO_2$	$k_3 = 1 \times 10^{-11}$ cm^3 molec^{-1} s^{-1}
R4	$O + O_2 + M$	$\rightarrow O_3 + M$	$k_4 = 10^{-33}$ cm^6 molec^{-2} s^{-1}
R5	$O + NO_2$	$\rightarrow O_2 + NO$	$k_5 = 1.1 \times 10^{-11}$ cm^3 molec^{-1} s^{-1}
R6	$O + ClO$	$\rightarrow O_2 + ClO$	$k_6 = 4.2 \times 10^{-11}$ cm^3 molec^{-1} s^{-1}
R7	$O + O_3$	$\rightarrow O_2 + O_2$	$k_7 = 5.4 \times 10^{-16}$ cm^3 molec^{-1} s^{-1}
R8	$O_2 + h\nu$	$\rightarrow 2\ O$	J_O2 (s^{-1})
R9	$O_3 + h\nu$	$\rightarrow O + O_2$	J_O3 (s^{-1})

Preliminary Instructions and getting oriented

1. Download the Excel data file (spade_subset.xls) from the course website:
http://www.atmos.washington.edu/academics/classes/2010Q4/458/spade_subset.xls
(If you use MatLab, please let me know and I will provide a .mat file.)

2. The file should contain some ~25 different variable names with units. In particular you will find various mixing ratios (ppt → parts per trillion 10^{-12}; ppb → parts per billion 10^{-9}; ppm → parts per million 10^{-6}, etc…). Pressure, **Pres**, is in hPa and temperature, **temp** is in Kelvin. **Lat** is latitude in degrees North and **Lon** is the longitude in degrees East. In addition, the photolysis rates for $O_2 \rightarrow O+O$, $O_3 \rightarrow O(^3P)+O_2$, and $O_3 \rightarrow O(^1D)+O_2$ are also given as **J_O2**, **J_O3O1D**, and J**_O3O3P** in units of inverse seconds.

3. Using the pressure and temperature variables, create a number density vector called "M". Make sure it has units of molec cm^{-3}.

4. Calculate the mean value of the pressure array and determine what altitude the aircraft was typically flying at during the two days of flights. (Hint: Use your pressure and altitude vectors from problem set 1.)

5. The quantity **SZA** is solar zenith angle and is essentially a measure of the local solar time. We will use it as our fundamental time of day unit. A SZA = 0 indicates true solar noon with the sun directly overhead, a |SZA| > 90 implies twilight/night/dawn, etc. In separate figures, plot "**Lat**" and "**Lon**" vs **SZA**. Look on a map to determine the region of the Earth being sampled during the two flights.

Photochemical Overview

1. Separately plot OH, HO_2, NO, NO_2, and ClO as a function of SZA.

2. Describe and explain qualitatively both the general behavior of each species plotted, e.g. "increases with solar radiation given the source is from photolysis of X", and the behavior of one family member relative to another, e.g. "HO_2 reaches much larger/smaller concentrations than OH likely because…").

3. In the stratosphere, OH and HO_2 rapidly cycle between one another driven by reactions R1, R2 and R3.

a. Assuming steady-state for OH and HO_2, write an equation to calculate the [OH]/[HO_2] ratio in terms of rate constants (k_1, k_2, k_3) and the observed [O_3] and [NO] values.
b. Using this equation, compare your modeled [OH]/[HO_2] ratio to the observed ratio of [OH]/[HO_2]. Plot both the observed and modeled ratios as a function of SZA.
c. What is the role of NO_x in terms of the OH/HO_2 ratio?

Contributions to Ozone Loss

Using what we have learned in lecture, you will now determine which radical family is contributing most to the chemical destruction of stratospheric ozone the observed air masses.

1. First, we need to calculate the concentration of O atoms (in molec/cm^3), which was not measured on these flights. The main sources of O atoms are the photolysis of O_3 (R9) and of O_2 (R8) and the main sink is reaction R4. You have estimates of the necessary photolysis rate constants in the excel sheet. Plot your O atom number density versus sza. Does it behave as expected? Is the magnitude reasonable given values in lecture and the textbook?

2. Write expressions for the loss rates of odd-oxygen (Ox) via HOx, NOx, ClOx, and Ox chemistry. Remember that the rate limiting steps are reactions R2, R5, R6, and R7, respectively. Using your O atom number density calculation, create four vectors (columns in excel): hox_o3_loss_rate, nox_o3_loss_rate, clox_o3_loss_rate, ox_o3_loss_rate. In addition, create a fifth vector: total_o3_loss_rate, which is the sum of the four vectors. Plot all five vectors with units of ppb per day vs sza (for |sza|<85).

3. Now determine which radical family controls O_3 destruction in this region of the stratosphere by plotting the four loss rates normalized to the total loss rate versus sza. It would be best to plot all four on the same graph.

4. What is the most important radical family in terms of O_3 destruction? What does this result say about Chapman's mechanism? How does this result compare to what we learned in class.

To learn more: Wennberg, P.O., et al., Removal of Stratospheric O_3 by Radicals: In Situ Measurements of OH, HO_2, NO, NO_2, ClO, and BrO, *Science,* **266**, 398-404, 1994.