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

Problem Set #3 (300 Points for 433 and 633)

Due: April 6, 2017 (at start of class)

Late penalty: *10 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: Wednesday, 12 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 (80 Points)

The Montreal Protocol has banned the industrial production of Halon-1301 (CF_3Br), which had been used to extinguish fires, as well as CFC-113 ($C_2Cl_3F_3$), which had been used as a refrigerant, foaming agents, and solvent:

http://ozone.unep.org/en/handbook-montreal-protocol-substances-deplete-ozone-layer/44

Industry has proposed N-propyl bromide ($CH_2BrCH_2CH_3$, or N-pb) is a solvent that has been proposed as a suitable replacement for CFC-113 ($C_2Cl_3F_3$).

Here we will examine the loss frequencies of Halon-1301 and N-pb compounds near the surface and in the stratosphere and will then consider public if the public policy is reasonable.

a) (20 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/spr2017/problem_sets/TableA.txt

www.atmos.umd.edu/~rjs/class/spr2017/problem_sets/TableB.txt

or (same info in excel format):

www.atmos.umd.edu/~rjs/class/spr2017/problem_sets/TableA.xls

www.atmos.umd.edu/~rjs/class/spr2017/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.

Compute the J value (photolysis frequency) for the two 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
$J_{Halon-1301}$		
J_{N-pb}		

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 270 K and a value of 1×10^6 molecules cm^{-3} for global mean tropospheric [OH], find the lifetime for removal of Halon-1301 and N-pb 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. As always, show your work.

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

http://www.atmos.umd.edu/~rjs/class/spr2017/problem_sets/JPL2015_Bimolecular_Rates.pdf

	Photolysis, 0 km	Reaction OH, troposphere	Photolysis, 40 km
$\tau_{Halon-1301}$			
τ_{N-pb}			

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 two 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) (20 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:

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

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

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

 iv) 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:

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

The loss of HO_x is equal to:

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

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:

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

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:

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

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/spr2017/problem_sets/JPL2015_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}, and the JPL 2015 expression for $k_{HO2+HO2}$ has two terms that must be evaluated and summed to get the appropriate, total rate constant.

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. (100 points) The Antarctic Ozone Hole. Here, we will examine the chemistry of Earth's polar stratosphere. Chlorine and bromine radicals are essential for understanding polar ozone depletion. An early indication that the Antarctic ozone hole is caused by measurements of ClO and O_3 was provide by measurements made by Dr. James Anderson and colleagues at Harvard University:

Anderson et al., *Science*, 1991
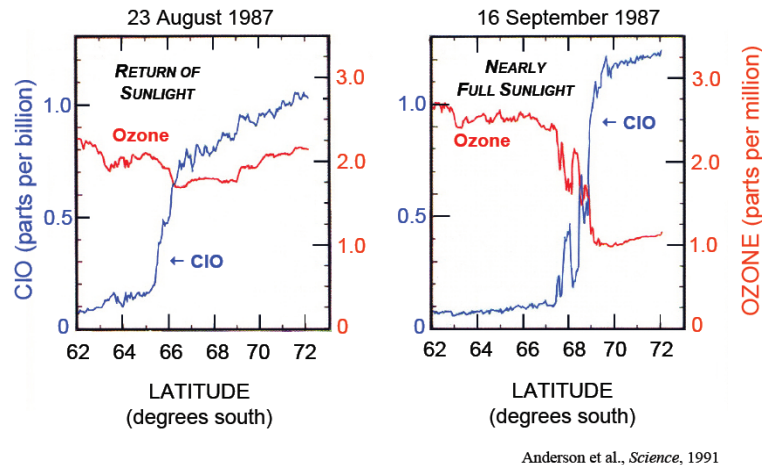
Indeed, these observations are so important they have been commemorated in a postage stamp, one of the few numismatic items that contain an actual scientific plot (complete with axes labels!):
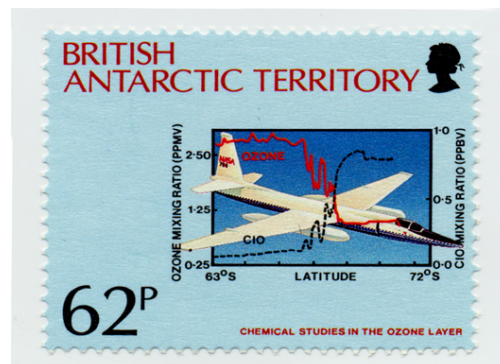
a) (20 points). Derive an expression for [ClOOCl]. In the Antarctic vortex, *when conditions are cold enough*, daytime loss of the chlorine monoxide dimer (ClOOCl) occurs only through photolysis:

$$ClOOCl + h\nu \rightarrow Cl + ClOO \tag{1}$$

ClOOCl is produced by the self reaction of ClO:

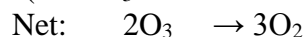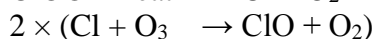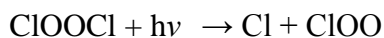$$ClO + ClO + M \rightarrow ClOOCl + M \tag{2}$$

Assuming ClOOCl is in steady state equilibrium (i.e., production and loss of ClOOCl are equal), **derive an expression for the concentration of [ClOOCl] in terms of [ClO], J_{ClOOl}, and $k_{ClO+ClO+M}$.**

b) (20 points) Evaluate [ClOOCl]. Using the expression for [ClOOCl] from part as well as information in the first four rows of the table below:

ClO $_{Noon}$	1.2 ppb
J$_{ClOOCl\text{-}noon}$	1.7×10^{-3} sec^{-1}
M	2.2×10^{18} molecule/cm^3
k$_{ClO+ClO+M}$	1.1×10^{-31} cm^6 / sec
T	187 K
BrO $_{Noon}$	12 ppt

find the value of [ClOOCl] at noon, in units of molecules/cm^3

c) (20 points) Chemical loss of ozone due to chlorine. Assuming ClOOCl is lost by photolysis, loss of ozone by the ClO+ClO cycle occurs through the following set of reactions reactions:

$$ClO + ClO + M \quad \rightarrow ClOOCl + M$$

$$ClOOCl + h\nu \rightarrow Cl + ClOO$$
$$ClOO + heat \rightarrow Cl + O_2$$
$$2 \times (Cl + O_3 \quad \rightarrow ClO + O_2)$$
$$Net: \quad 2O_3 \quad \rightarrow 3O_2$$

Since *two* ozone molecules are removed, we write:

Ozone Loss $_{ClO+ClO}$ = 2 J$_{ClOOCl}$ [ClOOCl]

Calculate **Ozone Loss** $_{ClO+ClO}$ at noon time and express the answer in units of parts per million per day.

d) (1 points) Refine chemical loss of ozone due to chlorine. The value of **Ozone Loss** $_{ClO+ClO}$ found above was based on a value for J$_{ClOOCl}$ and [ClO] appropriate for *noon* on 16 September, which is close enough to equinox to be consider equinox. Since ozone loss requires sunlight, refine your estimate of Ozone Loss $_{ClO+ClO}$ to represent sunlight conditions that prevailed over the 24 hour period on 16 September 1987by multiplying the value found in part C) by 0.5.

e) (20 points) Daily ozone rate loss due to coupled bromine chlorine reactions. As noted in class, bromine plays an important role in polar ozone loss. The reaction of BrO and ClO has three product channels:

$$BrO + ClO \rightarrow Br + ClOO \tag{3a}$$
$$\rightarrow BrCl + O_2 \tag{3b}$$
$$\rightarrow Br + OClO \tag{3c}$$

Only channels (3a) and (3b) lead to ozone loss. Assume that ozone loss by these two channels occurs at a rate of:

Ozone Loss $_{BrO+ClO}$ = 2 k_{3a} [BrO][ClO] + 2 k_{3b} [BrO][ClO]

Using the value for the appropriate rate constants from the table of bimolecular rates constants at:

http://www.atmos.umd.edu/~rjs/class/spr2017/problem_sets/JPL2015_Bimolecular_Rates.pdf

and values for [ClO]$_{noon}$ and [BrO]$_{noon}$ given above, find Ozone Loss $_{BrO+ClO}$. Please note that any quantity inside square brackets must be expressed using units of molecule/cm^3: i.e., you must convert the given mixing ratios for ClO and BrO to concentrations of ClO and BrO. Finally, as in part d) above, express your estimate of Ozone Loss $_{BrO+ClO}$ in units of parts per million /day.

f) (1 points). Refine chemical loss of ozone due to coupled bromine/chlorine cycle. The value of Ozone Loss $_{BrO+ClO}$ found above used a value for [BrO] and [ClO] appropriate for *noon* on 16 Sept. Since chemical loss of ozone by the coupled BrO/ClO cycle also requires sunlight, refine your estimate of Ozone Loss $_{BrO+ClO}$ to represent sunlight conditions that prevailed on 16 Sept 1987 by multiplying your estimate in part e) by 0.5.

g) (18 points). Can observed ClO explain the ozone hole: i.e. are the abundance of ClO and BrO measured in the Antarctic vortex on 16 September 1987 consistent with the change of O$_3$ that occurred between 23 August and 16 September 1987?

First, sum the values of Ozone Loss $_{ClO+ClO}$ and Ozone Loss $_{BrO+ClO}$ found in parts D and F to obtain Ozone Loss $_{TOTAL}$, in units of ppm / day.

Next, compute how much ozone changed, between 16 Sept and 23 Aug 1987, and from this change estimate the observed ozone rate of change, denoted Ozone Observed $_{LOSS\ RATE}$, again in units of ppm / day.

Is Ozone Loss $_{TOTAL}$ similar enough to Ozone Observed $_{LOSS\ RATE}$ for you to declare, in the upcoming press conference, that you have understood the cause of the ozone hole. If so, state the case and also (perhaps drawing on Lecture) state what aspect of the chemical systems still requires better quantification. If not, state the case and also (perhaps drawing on Lecture) state what other physical or chemical processes could be missing in our simple picture of polar ozone loss.