AOSC 433/633 & CHEM 633 Atmospheric Chemistry and Climate

Problem Set #4

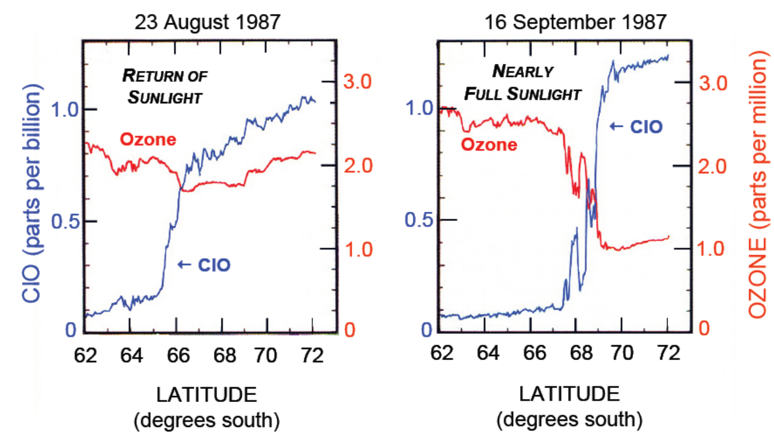
Due: Thursday, 9 April 2015

150 points

Please show all work. If you use a code to compute numerical values, attach a listing of the code, or if you use excel, attach (or email) the excel spread sheets.

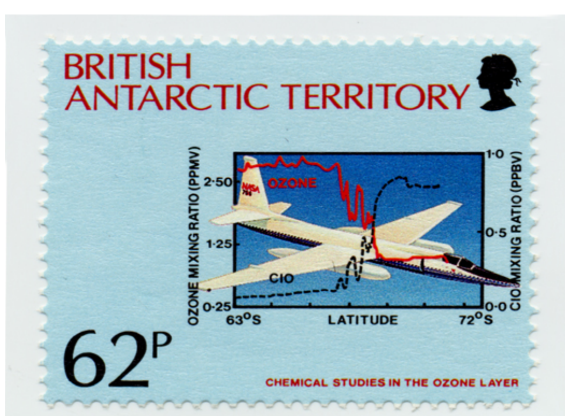
> ***Final deadline:*** Monday, 13 April 2015, 6:00 pm. No late penalty. But ***No Credit*** for submissions after this deadline because we will go over solutions in a review session on 13 April, 6:30 pm. Please get started early. As always, please see Austin, Tim, or Ross if you have questions or need assistance.

Here, we will examine the chemistry of Earth's polar stratosphere. As was seen in class, chlorine and bromine radicals are essential for understanding polar ozone destruction. 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:

$$ClOOCl + h\nu \rightarrow Cl + ClOO \qquad (1)$$

ClOOCl is produced by the self reaction of ClO:

$$ClO + ClO + M \rightarrow ClOOCl + M \qquad (2)$$

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].**

B. (20 points) Evaluate J_{ClOOCl}. Now we are going to guide you through an exercise designed to find a value for the abundance of the ClO dimer, [ClOOCl], given a value for [ClO]. To do this, we must ***first*** find the photolysis frequency of ClOOCl (J_{ClOOCl}). Using values for solar actinic flux and the absorption cross section for ClOOCl given in the table attached at the end of this problem set, which are for noontime conditions on 22 March, find J_{ClOOCl}.

The actinic flux and ClOOCl cross sections are available in electronic format at:

http://www.atmos.umd.edu/~rjs/class/spr2015/problem_sets/TableC.xls

and

http://www.atmos.umd.edu/~rjs/class/spr2015/problem_sets/TableC.txt

For this calculation, we will use the cross section for ClOOCl reported by Papanastasiou *et al.* 2009, which has been adopted by the latest JPL compendium.

C. (20 points) Evaluate [ClOOCl]. Using the expression for [ClOOCl] as a function of [ClO] from part A, the value for J_{ClOOCl} from part B, as well as the information in the table below, which is extracted from measurements inside the polar vortex obtained on 16 September 1987 under nearly full sunlight conditions.

ClO_{Noon}	1.2 ppb
T	187 K
M	2.2×10^{18} molecule/cm^3
$k_{ClO+ClO+M}$	1.1×10^{-31} cm^6 / sec
BrO_{Noon}	12 ppt

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

D. (20 points) Chemical loss of ozone due to chlorine. Chemical loss of ozone by the ClO+ClO cycle occurs through the following reactions

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

Since ClOOCl can be lost either by photolysis or by thermal decomposition, the photolysis rate of ClOOCl is the rate limiting step for ozone loss through this sequence of reactions. Since ***two*** ozone molecules are lost each time ClOOCl is lost by photolysis, we write:

$$\text{Ozone Loss}_{ClO+ClO} = 2\, J_{ClOOCl}\, [ClOOCl]$$

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

E. (10 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 198.

F. (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:

$$BrO + ClO \rightarrow Br + ClOO \quad (3a)$$
$$\rightarrow BrCl + O_2 \quad (3b)$$
$$\rightarrow Br + OClO \quad (3c)$$

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

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

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

http://www.atmos.umd.edu/~rjs/class/spr2015/problem_sets/JPL2010_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.

G. (10 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.

H. (20 points). Can observed ClO explain the ozone hole: i.e. is the abundance of ClO 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 E and G 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.