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

Problem Set #4

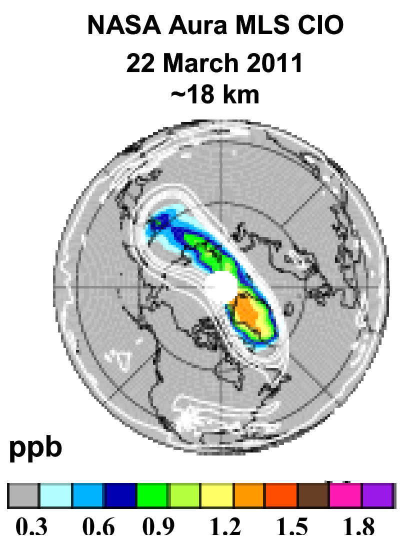
Due: Tuesday, 9 April 2013

155 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:*** Wednesday, 10 April 2013, 6:00 pm. No late penalty. But ***No Credit*** for submissions after this deadline because Allison will go over solutions in a review session on 10 April, 6:30 pm. Please get started early. As always, please see Allison, Tim, or Ross if you have questions or need assistance.

1. Arctic Ozone. This problem is motivated by the unusual conditions in the Arctic polar vortex that took place during spring 2011. Observations of ClO near 18 km altitude, as recorded by the Microwave Limb Sounder (MLS) instrument on the NASA Aura satellite, showed elevated levels of [ClO] near 18 km altitude last March:



A. (20 points). Derive an expression for ClOOCl. In the Artic vortex, ***when conditions are cold enough***, daytime loss of the chlorine monoxide dimer (ClOOCl) occurs only through photolysis:

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

ClOOCl is produced by the self reaction of ClO:

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

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/spr2013/problem_sets/TableC.xls

and

http://www.atmos.umd.edu/~rjs/class/spr2013/problem_sets/TableC.txt

Please use the cross section for ClOOCl reported by Papanastasiou *et al.* 2009 (students enrolled in 633 will later work with the other cross sections).

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:

ClO_{Noon}	1.3 ppb
T	188 K
M	2.3×10^{18} molecule/cm^3
$k_{ClO+ClO+M}$	8.3×10^{-32} cm^6 / sec
BrO_{Noon}	14 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, 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 22 March. Since ozone loss requires sunlight, refine your estimate of Ozone Loss $_{ClO+ClO}$ to represent sunlight conditions that prevail over the 24 hour period on 22 March 2011.

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:

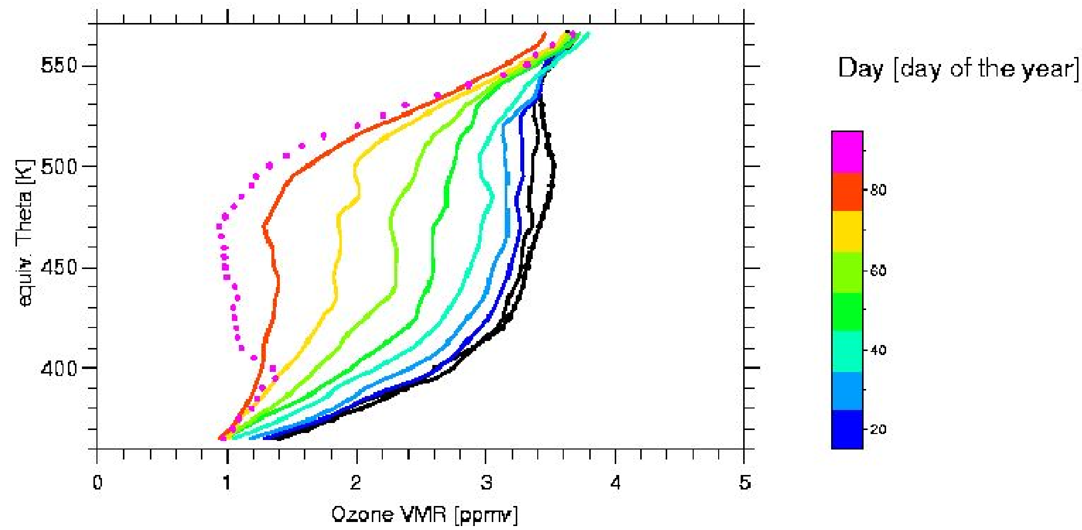
http://www.atmos.umd.edu/~rjs/class/spr2013/problem_sets/JPL2010_Bimolecular_Rates.pdf

and values for $[ClO]_{noon}$ and $[BrO]_{noon}$ given above, find 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 22 March. 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 prevail on 22 March 2011.

H. (10 points). Explain why a factor of 2 appears in the expression for Ozone Loss $_{BrO+ClO}$ and why the rate constant for channel (3c) does not appear.

I. (25 points). Assess the numbers. The figure below shows the evolution of ozone profiles in the Arctic vortex during the winter and spring of 2011:



The calculation you have conducted is for 22 March 2011, the 81st day of the year.

Based on your estimate of Ozone Loss $_{\text{Total}}$ = Ozone Loss $_{\text{ClO+ClO}}$ + Ozone Loss $_{\text{BrO+ClO}}$, assess how long it would have taken for ozone levels to reach zero within the Arctic polar vortex for spring 2011.

Assume your estimate applies at the **450 K** equivalent Theta level of this figure … equivalent Theta is a height coordinate that accounts for descent of air parcels through the polar winter season.

What meteorological development within the Arctic polar vortex could effectively stop chemical loss of ozone ***and*** why would chemical loss be stopped once this development occurred?

2. Graduate Students Only (150 points): The importance of ClOOCl photolysis

This question is assigned ***only to the students*** enrolled in 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*. Sorry but if we were to give extra credit, then the problem would no longer be exclusively assigned to 633. We do not expect most students enrolled in 433 to work this problem. But should anyone do so, we will gladly comment on your solution.

A. (50 points) Find [ClO] and [ClOOCl] given [ClO_x]. There has been considerable debate within the scientific community regarding the true value of the ClOOCl absorption cross section. Here, we ask you to calculate [ClO] and [ClOOCl], given [ClO_x], where ClO_x = [ClO] + 2 × [ClOOCl].

Assume the following conditions apply:

ClO_x	1.9 ppb
T	188 K
M	2.3×10^{18} molecule/cm^3
$k_{ClO+ClO+M}$	8.3×10^{-32} cm^6 / sec
BrO_{Noon}	14 ppt

Calculate the abundance of [ClO] and [ClOOCl] at noon, using all three values of the ClOOCl absorption cross section given in the table at the end of the problem set, available also at:

http://www.atmos.umd.edu/~rjs/class/spr2013/problem_sets/TableC.xls

and

http://www.atmos.umd.edu/~rjs/class/spr2013/problem_sets/TableC.txt

To complete this part of the problem, you will have to use algebraic manipulation of the expression used for Question 1 and the definition of ClO_x, leading to a quadratic equation for [ClO].

B. (50 points) Find Ozone Loss $_{\textbf{Total}}$. Estimate values of Ozone Loss $_{Total}$ for each value of the ClOOCl absorption cross section, refined (as above) to represent sunlight conditions that prevailed during the 24 hour period of time on 22 March 2011.

C. (25 points) Importance of ClOOCl absorption cross section. Comment on the importance of the ClOOCl absorption cross section for model estimates of chemical loss of polar ozone.

D. (25 points) Further Interpretation. Assuming the upper limit for ClO_x of 3.4 ppb (i.e., all chlorine is activated) and that [ClO] and [ClOOCl] are really governed by the equations we have used, which value of the ClOOCl cross section is ***least consistent*** with the MLS observations of ClO.

Wavelength range (nm)	Flux (photons cm^{-2} s^{-1})	JPL 2006 Cross Sections (cm^2)	Pope et al. 2007 Cross Sections (cm^2)	Papanastasiou et al., 2009 Cross Sections (cm^2)
202.5-207.5	2.00E+08	3.123E-18	0.000E+00	3.469E-18
207.5-212.5	8.57E+07	2.524E-18	0.000E+00	2.781E-18
212.5-217.5	6.13E+06	2.136E-18	0.000E+00	2.341E-18
217.5-222.5	7.92E+04	2.148E-18	0.000E+00	2.349E-18
222.5-227.5	3.21E+02	2.665E-18	7.690E-19	2.982E-18
227.5-232.5	5.82E-01	3.665E-18	3.376E-18	4.253E-18
232.5-237.5	1.12E-03	4.918E-18	4.774E-18	5.856E-18
237.5-242.5	6.70E-06	5.967E-18	5.947E-18	7.143E-18
242.5-247.5	1.78E-07	6.385E-18	6.354E-18	7.532E-18
247.5-252.5	1.23E-08	6.072E-18	5.863E-18	6.941E-18
252.5-256.2	4.97E-09	5.384E-18	4.973E-18	5.943E-18
256.2-260.0	1.58E-08	4.634E-18	4.111E-18	4.955E-18
260.0-265.0	1.75E-07	3.748E-18	3.207E-18	3.911E-18
265.0-270.0	7.80E-06	2.896E-18	2.475E-18	3.026E-18
270.0-275.0	1.82E-03	2.339E-18	1.957E-18	2.407E-18
275.0-280.0	7.81E-01	1.897E-18	1.562E-18	1.933E-18
280.0-285.0	7.16E+02	1.573E-18	1.234E-18	1.546E-18
285.0-290.0	7.83E+05	1.274E-18	9.584E-19	1.223E-18
290.0-295.0	3.99E+08	1.029E-18	7.304E-19	9.606E-19
295.0-300.0	1.28E+10	8.088E-19	5.458E-19	7.495E-19
300.0-305.0	9.94E+11	6.472E-19	3.994E-19	5.867E-19
305.0-310.0	2.28E+13	4.974E-19	2.858E-19	4.655E-19
310.0-315.0	1.27E+14	3.790E-19	1.975E-19	3.758E-19
315.0-320.0	3.18E+14	2.860E-19	1.338E-19	3.105E-19
320.0-325.0	5.56E+14	2.304E-19	8.835E-20	2.595E-19
325.0-330.0	8.30E+14	1.814E-19	5.642E-20	2.225E-19
330.0-335.0	9.48E+14	1.534E-19	3.522E-20	1.922E-19
335.0-340.0	1.02E+15	1.298E-19	2.185E-20	1.659E-19
340.0-345.0	1.07E+15	1.138E-19	1.408E-20	1.428E-19
345.0-350.0	1.09E+15	9.280E-20	9.490E-21	1.210E-19
350.0-355.0	1.15E+15	7.520E-20	6.940E-21	1.012E-19
355.0-360.0	1.14E+15	5.860E-20	4.360E-21	8.294E-20
360.0-365.0	1.23E+15	4.540E-20	2.760E-21	6.675E-20
365.0-370.0	1.40E+15	3.560E-20	1.791E-21	5.358E-20
370.0-375.0	1.36E+15	2.880E-20	1.162E-21	4.254E-20
375.0-380.0	1.38E+15	2.260E-20	7.543E-22	3.357E-20
380.0-385.0	1.32E+15	1.860E-20	4.895E-22	2.642E-20
385.0-390.0	1.32E+15	1.460E-20	3.177E-22	2.094E-20
390.0-395.0	1.34E+15	1.180E-20	2.061E-22	1.683E-20
395.0-400.0	1.70E+15	9.380E-21	1.338E-22	1.386E-20
400.0-405.0	2.20E+15	7.660E-21	8.681E-23	1.164E-20
405.0-410.0	2.29E+15	6.080E-21	5.634E-23	1.004E-20
410.0-415.0	2.40E+15	4.920E-21	3.656E-23	8.678E-21
415.0-420.0	2.46E+15	3.900E-21	2.372E-23	7.514E-21
420.0-425.0	2.42E+15	3.140E-21	1.540E-23	6.638E-21
425.0-430.0	2.23E+15	2.540E-21	9.991E-24	5.768E-21
430.0-435.0	2.34E+15	2.060E-21	6.484E-24	5.012E-21
435.0-440.0	2.55E+15	1.620E-21	4.207E-24	4.355E-21
440.0-445.0	2.67E+15	1.300E-21	2.730E-24	3.784E-21
445.0-450.0	2.88E+15	1.020E-21	1.772E-24	3.288E-21