ATM S 558
Problem Set #2 (see both sides)
Due: Wednesday April 20, 2011

I. The Montreal Protocol (based on problem 3.7 in the text)

The 1987 Montreal protocol was the first international agreement to control emissions of chlorofluorocarbons (CFCs) harmful to the ozone layer. It was subsequently amended (London 1990, Copenhagen 1992) to respond to the increased urgency created by the Antarctic ozone hole. In this problem we compare the effectiveness of the original and amended protocols. We focus on CFC-12, which has an atmospheric lifetime of 100 years against loss by photolysis in the stratosphere. We start our analysis in 1989 when the Montreal protocol entered into force. In 1989 the mass of CFC-12 in the atmosphere was $m = 1.0 \times 10^{10}$ kg and the emission rate was $E = 4 \times 10^{8}$ kg yr^{-1}.

a. The initial Montreal protocol called for a 50% reduction of CFC emissions by 1999 and a stabilization of emissions henceforth. Consider a future scenario where CFC-12 emissions are held constant at 50% of 1989 values. Show that the mass of CFC-12 in the atmosphere would eventually approach a steady-state value $m = 2 \times 10^{10}$ kg, higher than the 1989 value. Explain briefly why the CFC-12 abundance would increase even though its emission decreases. Using a software of your choice, calculate and plot the time-dependent evolution of the mass of CFC-12 in the atmosphere between 1989 and 2200.
b. The subsequent amendments to the Montreal protocol banned CFC production completely as of 1996. Consider a scenario where CFC-12 emissions are held constant at $E = 4 \times 10^{8}$ kg yr^{-1} from 1989 to 1996 and then ddrop to zero as of 1996. Calculate the masses of CFC-12 in the atmosphere in years 2050 and 2100. Compare to the 1989 value. Plot the resulting time-dependent evolution of CFC-12 in the atmosphere.
c. What would have happened if the Montreal protocol had been delayed by 10 years? Consider a scenario where emissions are held constant $E = 4 \times 10^{8}$ kg yr^{-1} from 1989 to 2006 and then drop to zero as of 2006. Calculate the masses of CFC-12 in the atmosphere in years 2050 and 2100. Briefly conclude as to the consequences of delayed action. Plot the results and compare to the scenarios outlined in a. and b.

II. Problem 10.8 in text

III. Evaluating the ClO-dimer mechanism for polar ozone loss

1. $ClO + ClO + M \rightarrow ClOOCl + M$ $k_1 = 1x10^{13}$ cm^3 $molec^{-1}$ s^{-1}
2. $ClOOCl + h\nu \rightarrow 2Cl + O_2$ $k_2 = 0.0015$ s^{-1}
3. $Cl + O_3 \rightarrow ClO + O_2$ $k_3 = 8x10^{-12}$ cm^3 $molec^{-1}$ s^{-1}

a. Calculate the lifetimes of Cl, ClO, and ClOOCl based on the above reactions. Assume that [ClO] = 1 ppb, [O_3] = 3 ppm, and [M] = $1.2x10^{18}$ molec cm^{-3}. (Note, k_1 is technically pressure dependent, but the role of [M] has already been included in the value of k_1.)

b. Based on the above timescales, estimate the O_3 destruction rate by the above mechanism. Approximately how many days until O_3 is completely destroyed in this region? How does this value compare to that quoted by Solomon, Reviews of Geophysics, 37, 3, 1999?

c. Not all of the ClO dimer (ClOOCl) undergoes photolysis, some actually decomposes back to ClO: i.e. reaction 4. $ClOOCl \rightarrow 2ClO$, where $k_4 = 2x10^{-6}$ at 190K and increases by a factor of ~10 per 10K increase in temperature. What is the effect of this reaction on ozone depletion? How important is this effect in the region and time period where the most significant polar ozone depletion occurs?