12.806 / 10.571 Atmospheric Physics and Chemistry
(Distributed April 4, 2006 and due April 11, 2006)

Problem 1

Say you are downwind from a large SO_2 "source region" in which the SO_2 concentration $[SO_2]$ (0) is 3 x 10^{11} molecule cm^{-3} in the lowest h kilometers and zero above that. There are no additional sources between you and this source region and the wind vector is horizontal (x direction) and constant in time. Assume that SO_2 is removed by reaction with OH in the gas phase to produce H_2SO_4. Derive a formula for P (= the rate of production per unit area of H_2SO_4) in the downwind region as a function of h, τ = SO_2 chemical lifetime = $1/l$ [OH] [M], l = third order rate constant, u = wind speed, and x = distance from source region. State briefly the major assumptions used in deriving your formula.

Graph P as a function of x from 0 km to 1000 km from the source for u = 3.3 m/sec, h = 1.9 km, l = 2 x 10^{-31} cm^6 $molecule^{-2}$ sec^{-1}, and [OH] = 2 x 10^6 radicals cm^{-3}. Compare this P graph to that computed for u = 7 m/sec and comment on the difference.
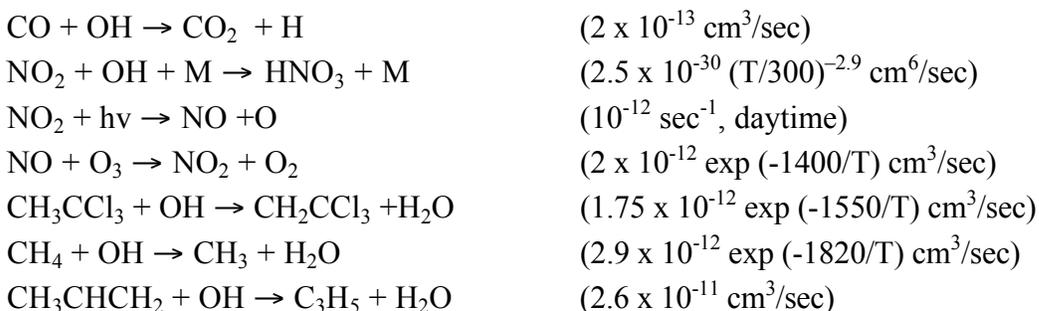
Problem 2

In mid-1992 the $CFCl_3$ and CF_2Cl_2 mole fractions at and below 15 km altitude were 298 x 10^{-12} molecules/cm^3 and 521 x 10^{-12} molecules/cm^3, respectively. You are given the following:

Altitude Range (km)	K_z (cm^2 sec^{-1})	J (sec^{-1}) $CFCl_3$	J (sec^{-1}) CF_2Cl_2
0–15	1.2 x 10^5	0	0
15–25	1.8 x 10^3	2 x 10^{-8}	6 x 10^{-9}
25–40	1.3 x 10^4	7 x 10^{-7}	8 x 10^{-8}
40–50	4.2 x 10^4	4 x 10^{-6}	5 x 10^{-7}

By solving the steady-state horizontally-averaged continuity equations for each species in each atmospheric layer compute and graph their mixing ratios as a function of altitude. (Assume H = 7.8 km at all altitudes.)

Problem 3

You are constructing a 3-D tropospheric chemical transport model and have chosen grid spacings of 150 km in the horizontal and 1.6 km in the vertical and a time step consistent with a Courant number of 0.1. Typical wind velocities are 3.2 m/sec in the horizontal and 0.7 cm/sec in the vertical. Also, $[O_3] \sim 10^{12}$ cm^{-3}, $[OH] \sim 10^6$ cm^{-3} (daytime only), $[M] \sim$ 1.7 x 10^{19} cm^{-3}, and T $\sim$ 276 K. Consider the following reactions whose approximate rate constants are given in parentheses:

$CO + OH \rightarrow CO_2 + H$	(2 x 10^{-13} cm^3/sec)
$NO_2 + OH + M \rightarrow HNO_3 + M$	(2.5 x 10^{-30} (T/300)$^{-2.9}$ cm^6/sec)
$NO_2 + hv \rightarrow NO + O$	(10^{-12} sec^{-1}, daytime)
$NO + O_3 \rightarrow NO_2 + O_2$	(2 x 10^{-12} exp (-1400/T) cm^3/sec)
$CH_3CCl_3 + OH \rightarrow CH_2CCl_3 + H_2O$	(1.75 x 10^{-12} exp (-1550/T) cm^3/sec)
$CH_4 + OH \rightarrow CH_3 + H_2O$	(2.9 x 10^{-12} exp (-1820/T) cm^3/sec)
$CH_3CHCH_2 + OH \rightarrow C_3H_5 + H_2O$	(2.6 x 10^{-11} cm^3/sec)

(a) For each of the gases CO, NO, NO_2, CH_3ClCl_3, CH_4 and CH_3CHCH_2, compute their chemical lifetimes and thus determine whether transport must be considered or whether a pure photochemical steady state (chemical production=chemical loss) can be assumed. Form chemical families where appropriate.

(b) A steady horizontal wind with a speed of 4.1 m/sec is blowing directly from an urban source region to a rural observing site 400 km downwind. The concentration of the gaseous hydrocarbon propene (CH_3CHCH_2) is observed to be 19 times less at the rural observing site than at the urban source region. Given the rate constant for reaction of OH with propene is 2.6 x 10^{-11} cm^3/sec, and assuming that this reaction is the only destruction mechanism for propene, calculate the average concentration of OH in the region between the source and observing site.

Using this calculated [OH] and the rate constants for reactions with OH from part (a), compute the factors by which the concentrations at the source and observing site will differ for CO, NO_2, CH_3CCl_3, and CH_4 (assume the air temperature T $\sim$ 292K).