Exercises

A. Consider the four Lagrangian simulations of air quality in a polluted city in the Excel file entitled simulations.xls on the homework web page for the course.

ex1.out - base case
ex1NOx.out (NO_x emissions reduced by 50% relative to base case)
ex1VOC.out (VOC emissions reduced by 50% relative to base case)
ex1both.out (NO_x and VOC emissions reduced by 50% relative to base case)

Which simulations violate the very old EPA limit of a 1-hour average in excess of 120 ppbv? Which simulations violate the pending EPA limit of an 8-hour average in excess of 75 ppbv?

B. By comparing the various simulations listed in Exercise A, determine whether ex1.out corresponds to a VOC- or NO_x-limited regime.

C. i) If toluene is present at 1.0 ppbC at ground level (298 K and 1 atm), what is its concentration in molecules cm^{-3}?
ii) If n-butanol is present at 1.0 ppbC at 285 K and P_{total}= 0.95 atm, what is its concentration in molecules cm^{-3}?
iii) Convert [isoprene] = 5×10^{10} molecules cm^{-3} at 298 K and 1 atm to ppbC.

D. The deposition velocity of O_3 is ~0.8 cm/sec and that of $HONO_2$ is ~3.5 cm/sec.
Using the concentration data in the file simulations.xls, compute the rate of loss of both species (in ppbv/hour) at 1500 in ex1.out, assuming the air mass is well mixed up to 1350 meters.
Compute the rate of loss of both species in % per hour

E. Use numerical integration with calculate the extent of $HONO_2$ formation over a 14-hour day assuming (unreasonably!) constant values of :

310 K and 0.99 atm
$[OH] = 3 \times 10^6$ molecule cm^{-3}
$[NO_2] = 1.5 \times 10^{11}$ molecule cm^{-3}

F. From the results in ex1.out:
Compute the **net** rate of ozone production at 1200 sec by numerical differentiation.

Problems

1. Below is a table showing the maximum [ozone] in cases C-G and in ex1.out.

Each of cases C-G reduces emissions of one class of VOC (or one VOC, in the case of HCHO) by the same number of ppbC.

Model	Max 1 hour [ozone] (ppbv)
Ex1 (base case)	169.2
D cut HC8 (C8 and larger alkanes)	168.0
E cut OLI (internal olefins)	162.1
F cut XYL (xylene)	162.1
G cut HCHO ($H_2C{=}O$)	144.4

Questions:

How do differences in rate constants[a] for OH + VOC reactions or photolysis cause the ozone reductions to be very small in some cases and large in others?

How does mechanism[b] cause the ozone reductions to be very small in some cases and large in others, in ways that can't be explained by the rate constant for OH + VOC?

Type of Answer: Qualitative or quantitative argument based on the efficiency of termination versus propagation.

(a) Since the cuts are equal in ppbC, the rate constants should be compared in units of in $ppmC^{-1}$ min^{-1} as in the mechanism file, not in units of cm^3 $molecule^{-1}$ sec^{-1}. Note that photolysis rate constant for formaldehyde is about 10^{-4} sec-1 hours at noon.

(b) Use the abbreviated chemical mechanism in the file Example-1-Reactions.pdf from the homework page of the course website. To get a better sense of what is going on in this mechanism, consider reaction 88:

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88 ETHP + NO ------> ALD + HO2 + NO2
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This one line represents two reactions:

$CH_3CH_2OO + NO \rightarrow CH_3CH_2O + NO_2$ (slow)

$CH_3CH_2O + O_2 \rightarrow CH_3CH{=}O + HOO + NO_2$ (fast)