

## 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<sub>x</sub> emissions reduced by 50% relative to base case)

ex1VOC.out (VOC emissions reduced by 50% relative to base case)

ex1both.out (NO<sub>x</sub> 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<sub>x</sub>-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<sup>-3</sup>?

ii) If n-butanol is present at 1.0 ppbC at 285 K and P<sub>total</sub> = 0.95 atm, what is its concentration in molecules cm<sup>-3</sup>?

iii) Convert [isoprene] =  $5 \times 10^{10}$  molecules cm<sup>-3</sup> at 298 K and 1 atm to ppbC.

D. The deposition velocity of O<sub>3</sub> is ~0.8 cm/sec and that of HONO<sub>2</sub> 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<sub>2</sub> formation over a 14-hour day assuming (unreasonably!) constant values of :

310 K and 0.99 atm

[OH] =  $3 \times 10^6$  molecule cm<sup>-3</sup>

[NO<sub>2</sub>] =  $1.5 \times 10^{11}$  molecule cm<sup>-3</sup>

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 <sub>2</sub> C=O)	144.4

Questions:

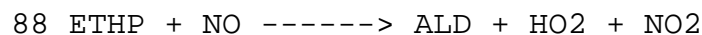
How do differences in rate constants<sup>a</sup> for OH + VOC reactions or photolysis cause the ozone reductions to be very small in some cases and large in others?

How does mechanism<sup>b</sup> 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<sup>-1</sup> min<sup>-1</sup> as in the mechanism file, not in units of cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>. Note that photolysis rate constant for formaldehyde is about 10<sup>-4</sup> sec<sup>-1</sup> 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:



This one line represents two reactions:

