Home Work Assignment Ozone Chemistry Part 1

1. Determine and compare the ozone photostationary state concentrations numerically and using the equation given in class for the initial conditions, \([\text{NO}]_0 = [\text{O}_3]_0 = 0.0 \text{ ppm}\), and for \([\text{NO}_2]_0\) of 0.1 ppm, 0.5 ppm, 1 ppm, and 5 ppm. Also include in a table the photostationary state concentrations of all gases involved in these reactions for each initial condition. Approximately how long does it take to reach steady state, provide a graph of the time evolution of NO, NO\(_2\), O\(_3\), and O for at least one numerical calculation. Is the steady-state concentration of [O] and the relationship between [NO] and [O\(_3\)] for these initial conditions as expected, explain why.

The reactions with rate constants are:

\[
\text{NO}_2 + \text{hv} = \text{NO} + \text{O}, \quad k_1 = 0.553 \text{ min}^{-1}
\]
\[
\text{O}_2 + \text{O} + \text{M} = \text{O}_3 + \text{M}, \quad k_2 = 2.183 \times 10^{-5} \text{ ppm}^{-2} \text{ min}^{-2}
\]
\[
\text{O}_3 + \text{NO} = \text{NO}_2 + \text{O}_2, \quad k_3 = 26.59 \text{ ppm}^{-1} \text{ min}^{-1}
\]

2. Solve the ODEs for the NO, NO\(_2\), CO system (see Table 4.2) for an ambient RH of 50%, \(T = 298 \text{ K}\) and 1 atm of pressure. Use initial conditions, \([\text{NO}]_0 = [\text{O}_3]_0 = 0\), and \([\text{NO}_2]_0 = 0.1 \text{ ppm}\). Investigate the time-dependant change in concentrations of O\(_3\) at the very beginning of the reactions (e.g., less than say 10 minutes) and over longer time scales (e.g., 600 minutes). Explain the results in a few sentences. Use a typical urban [CO] concentration.

3. Solve the ODEs for the HCHO system (see Table 4.3) in a batch reactor at a RH of 50%, \(T = 298 \text{ K}\), and 1 atm pressure and initial conditions \([\text{NO}_2]_0 = 0.1 \text{ ppm}\), \([\text{NO}]_0 = 0.01 \text{ ppm}\), and \([\text{HCHO}]_0 = 0.1 \text{ ppm}\). Plot the time dependant concentrations of NO, NO\(_2\), O\(_3\), and HCHO from 0 to 600 minutes. Explain in terms of the chemical reactions the behavior of these compounds by focusing on three regimes, 1) the initial few minutes, 2) from initial few minutes to about 300 minutes, and 3) the final 300 minutes. The rate constants for reaction 4a is 1.6E-3 min\(^{-1}\), and 4b is 2.11E-3 min\(^{-1}\).

4. Solve the ODEs for the HCHO system (see Table 4.3) in a batch reactor at a RH of 50%, \(T = 298 \text{ K}\), and 1 atm pressure and initial conditions \([\text{NO}_2]_0 = 0.1 \text{ ppm}\), \([\text{NO}]_0 = 0.1 \text{ ppm}\), and \([\text{HCHO}]_0 = 0.1 \text{ ppm}\). Plot the time dependant concentrations of NO, NO\(_2\), O\(_3\), and HCHO from 0 to 600 minutes. Then plot the concentration of these species if the lights are shut off at 1) 5 min, and 2) 80 min.
into the reaction (you will have a total of four graphs). Explain the behavior of the system.

5. Using the general results of question 4), or if you wish, other numerical simulations, can you explain why at night over urban regions near-surface $[O_3]$ are close to zero, but aloft they are not.