PHYS/OCEA 4595 Atmospheric Chemistry Quiz 3, December 2, 2019

Helpful Constants:

1 hPa = 100 Pa = 100 N/m^2

Na = 6.02×10^{23} molecules/mole

1. In the troposphere, O^1D production occurs in a very narrow wavelength interval between 300 and 320 nm.

(i) What is the main reason that O^1D production is very low for $\lambda > 320$. (3 points)

(ii) What is the main reason that O^1D production is very low for $\lambda < 300$. (3 points)

2. What are two important sources of CO to the troposphere? (4 points)

3. What is the main sink of CO in the troposphere? (2 points)

4. In the tropical troposphere, the OH concentration is largest in the mid-troposphere. Explain why the OH concentration decreases toward the upper troposphere and toward the surface. (6 points)

5. CH_4 is an important greenhouse gas not only by itself, but also because of other changes to atmospheric chemical composition that occur because of methane oxidation. Specify two of these changes that affect the radiative forcing. (6 points)

6. Suppose there were no anthropogenic emissions of NO_x, but anthropogenic emissions of all other species were unchanged. How would OH concentrations respond? Explain. Reference to specific reactions would be helpful. (6 points)

7. The HO_x and NO_x radical subfamilies mainly destroy ozone in the stratosphere, but usually contribute to ozone production in the troposphere. What is the main reason for this difference? Explain with reference to specific reactions if possible. (4 points)

8. Satellite measurements show that the southeast United States has large concentrations of formaldehyde in summer. What is the main reason for this? (3 points)

9. On a per molecule basis, an NO molecule generated by lightning will usually generate more ozone than an NO molecule emitted near the surface in an urban area. Discuss the reasons for this. (3 points)

10. (i) Draw a contour plot of how ozone concentrations typically depend on emissions of NO_x (the x axis) and emissions of hydrocarbons (the y axis) in an urban area. (8 points)

(ii) In the diagram, show the boundary between the NO_x limited and hydrocarbon-limited regimes, and label the two regimes. (4 points)

(iii) In recent years, there has been an increased appreciation of the role of isoprene (a naturally emitted hydrocarbon) on ozone production in rural areas. Would increased isoprene tend to push ozone production into the NO_x or hydrocarbon limited regime? Explain with reference to the diagram. (4 points)

(iv) In the lecture notes, we discussed expressions for the limiting rate of ozone production in the two regimes. These expression were derived from specific assumptions about the main sinks of another chemical family. What is this chemical family, and what are the assumptions made for each limit? (6 points)

11. (i) Model the lower atmosphere over the United States as a well-mixed box extending horizontally 5000 km in the west-east direction. There is a constant westerly wind blowing air through the box at U = 10 m/sec. Assume the mean concentration of OH in the box is $[OH] = 1.2 \times 10^6\ molecules/cm^3$. Assume the following reactions, and that NO_x can be partitioned using family style approximations. (Remember NO_x = NO + NO_2.)

$NO_2 + OH \rightarrow HNO_3 \qquad k_1 = 1.0 \times 10^{-11}\, cm^3/molec - sec$
$NO + O_3 \rightarrow NO_2 + O_2 \quad k_2 = 9.2 \times 10^{-15}\, cm^3/molec - sec$
$NO_2 + h\nu \rightarrow NO + O \quad k_{NO_2} = 0.01\, sec^{-1}$
$O_3 : 50\, ppbv$
$[M] = 2 \times 10^{19}\, molec/cm^3$

(i) Derive an expression for the NO/NO_2 ratio. (12 points)

(ii) What is the lifetime of an NO_x (= NO + NO_2) molecule in the box against conversion to HNO_3 (in days)? (16 points)

(iii) What is the residence time of an air parcel in the box against removal by transport (in days)? (8 points)