PHYS/OCEA 4595 Atmospheric Chemistry Quiz 2, November 5, 2019

Helpful Constants:

1 hPa = 100 Pa = 100 N/m^2
gravitational acceleration g = 9.80 m/sec^2
radius of the earth R = 6400 km
mean molecular mass of air M_a = 28.96 g/mole
Na = 6.02×10^{23} molecules/mole
Transmission $= T = e^{-\delta}$

$\delta = n\sigma L = N\sigma$ (N in molecules/area, n in molecules/volume)

1. There are three aerosol regimes depending on the relative magnitudes of total sulphate, total ammonia, and total nitrate. Specify how the three regimes are defined, and the fraction of total ammonia and nitrate that is typically in the aerosol form for each. (8 points)

2. There are three main requirements for forming an ozone hole. Specify two of these. (4 points)

3. Specify two ways in which the presence of NO_x (= NO + NO_2) slows down rates of ozone destruction due to other catalytic cycles (either HO_x or ClO_x). In your discussion specify the relevant reactions. (6 points)

4. Suppose molecule A is dissociated by light with wavelengths less than 250 nm (far UV), while molecule B is dissociated by visible light. Roughly plot how the photolysis rates of A and B would be expected to depend on altitude, and indicate their relative magnitude. (6 points)

5. Assume that 1 percent of the incident top of the atmosphere solar flux at 300 nm reaches the ground. Also assume that the only significant absorber in the atmosphere at this wavelength is ozone, and that scattering can be neglected. The ozone absorption cross section at 300 nm is 34.3×10^{-20} cm^2 per molecule. The solar zenith angle is 60 ^{o} (from the vertical).

(i) What is the optical depth of the atmosphere at a solar zenith angle of 60 ^{o} from the vertical? (4 points)

(ii) What is the optical depth of the atmosphere for overhead sun? (4 points)

(iii) What is the column ozone amount in molecules per cm^2? (4 points)

(iv) What is the ozone column in Dobson Units? 1 Dobson Unit = 2.69×10^{16} molecules per cm^2. (2 points)

6. Derive the Chapman expression for the ozone concentration using the following steps. You may make all necessary family style approximations. Write $[O_2] = C_{O_2}[M]$, where $[M]$ is the total number density of the atmosphere (sometimes called n_a). Your final answer should express $[O_3]$ in terms of k_{O_2} (the ozone photolysis rate), k_{O_3} (the ozone photolysis rate), k_1, k_2, C_{O_2}, and $[M]$. Assume the following reactions:

k_{O_2} : $O_2 + hv \rightarrow O + O$
k_1 : $O + O_2 + M \rightarrow O_3 + M$
k_{O_3} : $O_3 + hv \rightarrow O_2 + O$
k_2 : $O + O_3 + M \rightarrow 2\ O_2$

(i) Derive an approximate expression for the $[O]/[O_3]$ ratio. (8 points)

(ii) Assume that odd oxygen ($[O_x]$) is in steady state. Use this constraint, and the result from (i) to derive the Chapman expression for the ozone concentration. (12 points)

(iii) Make a plot of the typical vertical variation of J_{O_2} as a function of height from the surface to 50 km. (6 points)

(iv) Make a plot of the typical vertical variation of $[O_3]$ as a function of height from the surface to 50 km as predicted by the Chapman expression. Explain the behavior at high and low altitudes. (8 points)

(v) What is the main failure of the Chapman expression for $[O_3]$? Explain the reasons for this failure. (6 points)

7. Consider the following reactions only:

$OH + O_3 \rightarrow HO_2 + O_2 \qquad k_1 = 2.0 \times 10^{-14}\, cm^3/molec - sec$

$HO_2 + O_3 \rightarrow OH + 2\,O_2 \qquad k_2 = 1.0 \times 10^{-15}\, cm^3/molec - sec$

$[M] = 2 \times 10^{18}\, molec/cm^3$.
OH = 0.6 pptv
O_3 = 4 ppmv

(i) HO_x destroys O_x in the stratosphere via a catalytic cycle. Specify the sequence of reactions in this cycle, and indicate how many O_x are destroyed. (6 points)

(ii) Assume that HO_x is a family. Obtain an expression for the $[OH]/[HO_2]$ ratio. (6 points)

(iii) Use this expression to calculate the $[HO_2]$ mixing ratio in pptv. (4 points)

(iv) What is the lifetime of an O_x (or ozone) molecule with respect to destruction by the ozone destroying HO_x cycle? (6 points)