**ATOC 3500/CHEM 3151**

**Problem 13**

**Week 7**

**Do Part (a) before class on February 27.**

**We will do parts b, c, and d in class.**

In class on Thursday, February 22, 2018, we saw that there were four reactions that could explain the presence of ozone in the stratosphere. These four reactions, listed below, were first described by Sydney Chapman, an atmospheric scientist who discovered many important properties of the upper atmosphere. A brief biography of Sydney Chapman can be found here:

http://onlinelibrary.wiley.com/doi/10.1029/2011EO340001/pdf

The four chemical equations Chapman proposed to explain the abundance of ozone are:

                                             O2 + h http://atoc.colorado.edu/~toohey/arrow.gif O + O                          Rate 1 = \_\_\_\_\_\_\_\_\_\_\_\_\_

                                             O + O2 + M http://atoc.colorado.edu/~toohey/arrow.gif O3 + M                  Rate 2 = \_\_\_\_\_\_\_\_\_\_\_\_\_

                                             O3 + h http://atoc.colorado.edu/~toohey/arrow.gif O + O2                         Rate 3 = \_\_\_\_\_\_\_\_\_\_\_\_\_

                                              O + O3 http://atoc.colorado.edu/~toohey/arrow.gif O2 + O2                        Rate 4 = \_\_\_\_\_\_\_\_\_\_\_\_\_

1. Using the following terms to fill in the right hand sides of the Rate expressions for each of the reactions above.

Rate constant for O2 photolysis, J1 = k1 x [h]

Rate constant for O3 photolysis, J3 = k3 x [h]

Rate constant for O + O2 + M, k2III

Rate constant for O + O3, k4II

1. Write two separate expressions for the rates of change of [O] and [O3] using the four reactions above (i.e., d[O]/dt = …. and d[O3]/dt = ….).
2. Note that there is no easy way to solve for [O] or [O3] and substitute back into the other equation that simplifies the expressions above. Therefore, Chapman considered a new term, the sum of [O] and [O3], which he called “[Ox]”. By summing the two expressions you found in Part (a), show that the right hand side of the expression below involves only reactions 1 and 4.

d[Ox]/dt = d[O]/dt + d[O3]/dt = Expression 1 + Expression 2

= \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

+ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

= \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

1. Solve the equation in Part (c) for [O] assuming that [Ox] is in steady state (i.e., d[Ox]/dt = 0).
2. Now, just for fun, assume that the rates of the second and third reactions in Chapman’s scheme are equal. Using a similar approach calculate the ratio of [O]/[O3]. Use J3 = 1x10-2 s-1 and k2 = 1x10-33 cm6 molecule-2 s-1. Do this calculation for densities of [M] = 2.0x1018 molecule cm-3 and [M] = 1.0x1017 molecule cm-3.

(e) At what altitude is the ratio of [O]/[O3] = 1? You can estimate the altitude (z) using the formula z = 7 ln(2.7x1019/[M]), which is from the barometric law, and where z is in km. Remember that [O2] = 0.21[M].