**ATOC 3500/CHEM 3151**

**Problem 14**

**Week 8-9**

**In Class March 15**

We have learned that Chapman chemistry (“oxygen reactions alone”) overpredicts observed abundances of ozone in the stratosphere. Because ozone production is fixed (the rate of oxygen photolysis depends on ultraviolet flux from the Sun, which is relatively constant), in the 1960s and 1970s atmospheric scientists realized there must be missing ozone destruction processes. This problem examines the role of chlorine in ozone loss in the global stratosphere (i.e., away from the polar regions).

The following reactions describe the pathways for rapid cycling of ‘reactive’ chlorine (Cl and ClO) in the upper stratosphere:

                                             Cl + O3  ClO + O2               Rate 1 = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

                                             ClO + O  Cl + O2                Rate 2 = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

                                             ClO + NO  Cl + NO2          Rate 3 = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

                                             NO2 + h  NO + O           Rate 4 = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

1. Fill in the right hand sides of the rate expressions for each of the reactions above.
2. Sum up the first two reactions to show that each time a chlorine atom cycles through these two reactions, two odd oxygens ([Ox] = O + O3) are destroyed.
3. Sum up reactions 1, 3 and 4 to show that each time a chlorine atom cycles through these two reactions, there is no change in odd oxygen.
4. Noting, therefore, that each time a chlorine atom cycles through reactions 1 and 2, two odd oxygens are lost, use the steady state [ClO] to write an expression for d[O3]/dt using:

d[O3]/dt = 2 k2 [ClO] [O] = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_