CHEMISTRY 253
Spring, 2015 - Dixon
Group Assignment #2

Group Names _KEY___

Stratospheric Chemistry Problem:
1. By carrying out a number of calculations or thought experiments, we can better understand the Chapman Mechanism chemistry involving ozone production and destruction.

The Chapman mechanism reactions are:
1) $O_2 + h\nu \rightarrow 2O$
2) $O + O_2 + M \rightarrow O_3 + M$
3) $O_3 + h\nu \rightarrow O_2 + O$
and 4) $O + O_3 \rightarrow 2O_2$

Additional Needed information: N_{Ava} = 6.02 x 10^{23} molec/mol and assume that >99% of O in stratosphere is in form O_2. [put on board]

Answer the following specific questions:
1. What does M refer to in step 2)? *any air molecule (just to remove extra kinetic energy)*

2. If the rate constant, k, for reaction 2 is 2 x10^{-33} cm^6 $molec^{-2}$ s^{-1}, calculate the lifetime of O atoms with respect to loss by reaction 2 at 25 km if P_{air} = 0.04 atm and $\%O_2$ by volume = 20%. Assume T = -40°C. R = 0.0821 L atm/mol K and 0°C = 273 K.
Hint: you can use the ideal gas law to get n/V in mol/L and then convert to molec cm^{-3}. The lifetime (in s) can be calculated as the ratio of the concentration (molec cm^{-3}) to the sink (molec O cm^{-3} s^{-1}), cancelling out [O] (since it is not given).
$\tau = [O]/\{d[O]/dt\} = [O]/\{k[O][O_2][M]\} = 1/\{k[O_2][M]\}$
$[M] = n/V = P_{air}/RT = 0.04$ atm/[(0.0821 L atm/mol K)(273 – 40K)] = 0.04 atm/(19.1 L atm/mol)
$[M] = (0.00209$ mol/L)(6.02 x 10^{23} molec/mol)(1L/1000 cm^3) = 1.26 x 10^{18} molec/cm^3
$[O_2] = 0.2[M] = 2.52$ x 10^{17} molec/cm^3
τ = 1/[(2 x10^{-33} cm^6 $molec^{-2}$ s^{-1})(1.26 x 10^{18} molec/cm^3)(2.52 x 10^{17} molec/cm^3)] = ***0.002 s***

3. Within the stratosphere, how will the lifetime of O with respect to reaction 2 depend on altitude?
It will decrease because [M] and $[O_2]$ decrease with altitude due to the decrease in P.

4. At night in the stratosphere, reactions 1 and 3 are stopped. Would you expect the concentration of O_3 to decrease to zero? What about the concentration of O atoms? You can assume that the concentration of O_3 is much higher than O atoms.
Sources of both O_3 and are stopped at night. Because reaction 2 is fast, O atoms will quickly be depleted and go to zero concentration. Once O atoms are gone, reaction 4 can't proceed and the ozone concentration will be constant (no source and no sink).