Atmospheric Chemistry: Quiz No. 1 Name:_____Exam Key_____

1. What process creates ozone in the stratosphere?

Photodissociation of O_2 ($h\nu + O_2 \rightarrow O + O$) followed by atomic oxygen combining with O_2 ($O + O_2 + M \rightarrow O_3 + M$)

2. Why is stratospheric ozone important to life at the surface of the Earth?

It absorbs solar radiation that can break bonds in DNA molecules (skin cancer; crop damage, etc.)

3. Write the 4 basic chemical reactions that describe the "pure oxygen" mechanism that determines the concentration of stratospheric ozone.

$h\nu + O_2 \rightarrow O + O$; *initiation/production*
$O + O_2 + M \rightarrow O_3 + M$; *chain propagation*
$h\nu + O_3 \rightarrow O_2 + O$; *chain propagation*
$O + O_3 \rightarrow O_2 + O_2$; *termination/loss*

4. What do we mean by the term "odd" oxygen? Why is it a useful concept?

$[O_x] = [O_3] + [O]$
Simplifies chemical equations; separates fast chemical reactions from slower chemical reactions

5. Which reactions in question 3 occur rapidly enough that we can assume a steady state to solve for the ratio of [O] to [O_3]? Write the expression for the ratio.

$O + O_2 + M \rightarrow O_3 + M$
$h\nu + O_3 \rightarrow O_2 + O$

loss of O atoms = production of O atoms $\rightarrow$
$k_{O,O2,M}[O][O_2][M]=J_{O3}[O_3]$

solve for $[O]/[O_3]=J_{O3}/k_{O,O2,M}[O_2][M]$

6. Using the ratio for [O] to [O_3] write the equation that determines the steady-state concentration of odd oxygen.

$d[O]/dt = 2 J_{02}[O_2] - k_{0,02,M}[O][O_2][M] + J_{03}[O_3] - k_{0,03}[O][O_3]$
$d[O_3]/dt = k_{0,02,M}[O][O_2][M] - J_{03}[O_3] - k_{0,03}[O][O_3]$

add these equations

$d([O]+[O_3])/dt = d[O_x]/dt = 2 J_{02}[O_2] - 2 k_{0,03}[O][O_3]$

Substitute ratio $[O]/[O_3]$ and set to zero for steady-state

$J_{02}[O_2] = k_{0,03}[O]/[O_3] [O_3]^2$

Solve for $[O_3]^2 = J_{02}[O_2]/(k_{0,03}[O]/[O_3])$

Take square root and substitute for $[O]/[O_3] \rightarrow [O_3] = [O_2] (J_{02} k_{0,02,M} [M]/(k_{0,03} J_{03}))^{1/2}$

7. What is meant by chemical lifetime? What is the expression for lifetime due to a) photolysis, b) two-body reaction, c) three-body reaction?

Chemical lifetime is time to reduce to 1/e of original concentration in the absence of production of the chemical species

a) $\tau = 1/J$

b) $\tau_A = 1/(k_{A,B} [B])$ *where [B] is density of species B that is reacting with species A*

c) $\tau_A = 1/(k_{A,B,M} [B][M])$ *where [B] is density of species B that is reacting with species A and M is third body necessary to conserve energy and momentum simultaneously*

8. What is chemical catalysis? Give an example (chemical reactions) for either NO_x or HO_x.

Catalysis occurs when a set of reactions causes a chemical species to be removed without loss of the catalyst.

Example: $NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + O \rightarrow NO + O_2$

The net result is $O + O_3 \rightarrow O_2 + O_2$ *; a loss of odd oxygen without using up the NO or* NO_2

9. What do we mean by the "rate-determining step?

For the case of NO_x catalysis for instance, the rate-determining step is the one that determines whether the cycle from NO to NO_2 and back results in catalysis. After NO reacts with O_3 we have NO_2, which can either recycle to NO without catalytic ozone loss by absorbing a photon or we can have catalytic loss by NO_2 reacting with atomic oxygen. The reaction with atomic oxygen is the rate-determining step for NO_x catalysis.

10. What is the expression for the lifetime of odd oxygen due to pure oxygen (O_x) reactions? What is the corresponding expression for the lifetime of odd oxygen due to catalytic reactions of NO_x? If we have both pure oxygen reactions and NO_x catalysis reactions, what is the expression for the lifetime of odd oxygen due to the combined loss processes?

$$d[O_x]/dt \text{ (due to } O_x) = -2\, k_{O,O3}\, [O][O_3] = -2\, k_{O,O3}\, ([O]/[O_3]\, [O_3])\, [O_3]$$

$$\tau_{Ox} \text{ (due to } O_x) = 1/(2\, k_{O,O3}\, ([O]/[O_3]\, [O_3])$$

$$d[O_x]/dt \text{ (due to } NO_x) = -2\, k_{O,NO2}\, [O][NO_2] = -2\, k_{O,O3}\, ([O]/[O_3]\, [NO_2])\, [O_3]$$

$$\tau_{Ox} \text{ (due to } O_x) = 1/(2\, k_{O,NO2}\, ([O]/[O_3]\, [NO_2])$$