

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<sub>3</sub>]? 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  $\rightarrow$*

*$k_{0,02,M}[O][O_2][M] = j_{03}[O_3]$*

*solve for  $[O]/[O_3] = j_{03}/k_{0,02,M}[O_2][M]$*

6. Using the ratio for [O] to [O<sub>3</sub>] write the equation that determines the steady-state concentration of odd oxygen.

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

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<sub>3</sub>] and set to zero for steady-state

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

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

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

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*

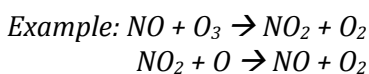
a)  $\tau = 1/J$

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<sub>x</sub> or HO<sub>x</sub>.

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



The net result is  $O + O_3 \rightarrow O_2 + O_2$ ; a loss of odd oxygen without using up the NO or NO<sub>2</sub>

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

*For the case of  $\text{NO}_x$  catalysis for instance, the rate-determining step is the one that determines whether the cycle from  $\text{NO}$  to  $\text{NO}_2$  and back results in catalysis. After  $\text{NO}$  reacts with  $\text{O}_3$  we have  $\text{NO}_2$ , which can either recycle to  $\text{NO}$  without catalytic ozone loss by absorbing a photon or we can have catalytic loss by  $\text{NO}_2$  reacting with atomic oxygen. The reaction with atomic oxygen is the rate-determining step for  $\text{NO}_x$  catalysis.*

10. What is the expression for the lifetime of odd oxygen due to pure oxygen ( $\text{O}_x$ ) reactions? What is the corresponding expression for the lifetime of odd oxygen due to catalytic reactions of  $\text{NO}_x$ ? If we have both pure oxygen reactions and  $\text{NO}_x$  catalysis reactions, what is the expression for the lifetime of odd oxygen due to the combined loss processes?

$$d[\text{O}_x]/dt \text{ (due to } \text{O}_x) = -2 k_{0,03} [\text{O}][\text{O}_3] = -2 k_{0,03} ([\text{O}]/[\text{O}_3] [\text{O}_3]) [\text{O}_3]$$

$$\tau_{\text{O}_x} \text{ (due to } \text{O}_x) = 1/(2 k_{0,03} ([\text{O}]/[\text{O}_3] [\text{O}_3]))$$

$$d[\text{O}_x]/dt \text{ (due to } \text{NO}_x) = -2 k_{0,\text{NO}_2} [\text{O}][\text{NO}_2] = -2 k_{0,03} ([\text{O}]/[\text{O}_3] [\text{NO}_2]) [\text{O}_3]$$

$$\tau_{\text{O}_x} \text{ (due to } \text{NO}_x) = 1/(2 k_{0,\text{NO}_2} ([\text{O}]/[\text{O}_3] [\text{NO}_2]))$$