Atmospheric Chemistry

Lecture 7
Ozone Continuity Equation with NO\textsubscript{x} and HO\textsubscript{x} Terms

\[
\frac{dO_x}{dt} = 2 \cdot J_{O_2} \cdot [O_2] - 2 \cdot k_{O,O_3} \cdot [O] \cdot [O_3] - 2 \cdot k_{O,NO_2} \cdot [O] \cdot [NO_2]
\]

\[-2 \cdot k_{O,HO_2} \cdot [O] \cdot [HO_2] - 2 \cdot k_{O_3,HO_2} \cdot [O_3] \cdot [HO_2] \]

Approximate Altitude (km)

Loss Rate Due to Each Cycle (10^{-6} \text{ cm}^{-3} \text{ sec}^{-1})

Fraction Loss Due to Cycle (%)
Recasting the \([O_x]\) continuity equation

\[
\frac{dO_x}{dt} = P_{O_x} - \kappa \cdot [O_3] - \alpha \cdot [ON] \cdot [O_3] - \beta \cdot [HO_x] \cdot [O_3]
\]

where:

\[
\alpha = 2 \cdot k_{O,NO_2} \cdot \frac{[O]}{[O_3]} \cdot \frac{[NO_2]}{[ON]}
\]

\[
\beta = 2 \cdot \left( k_{O_3,HO_2} + k_{O,HO_2} \cdot \frac{[O]}{[O_3]} \right) \cdot \frac{[HO_2]}{HO_x}
\]

\[
\kappa = 2 \cdot k_{O,O_3} \cdot \frac{[O]}{O_3} \cdot [O_3]
\]

\[
\frac{[O]}{[O_3]} = \frac{J_{O_3}}{k_{O,O_2,M} \cdot [O_2] \cdot [M]}
\]
“Odd” Nitrogen = ON

**NO\textsubscript{x}**

- N : nitrogen atom
- NO : nitric oxide
- NO\textsubscript{2} : nitrogen dioxide
- NO\textsubscript{3} : nitrogen trioxide
- N\textsubscript{2}O\textsubscript{5} : dinitrogen pentoxide

**Even Nitrogen**

- N\textsubscript{2} : molecular nitrogen
- N\textsubscript{2}O : nitrous oxide

**Reservoirs**

- HNO\textsubscript{3} : nitric acid
- HO\textsubscript{2}NO\textsubscript{2} : pernitric acid
- ClONO\textsubscript{2} : chlorine nitrate
- BrONO\textsubscript{2} : bromine nitrate
Daytime NO$_x$ Chemistry

- NO → NO$_2$ → N$_2$O$_5$
- NO → NO$_3$
- NO$_2$ → NO$_3$
- NO$_2$ → hν → O$_3$
- NO$_3$ → hν → O$_3$

Atmospheric Chemistry Lecture 7
Nighttime NO\textsubscript{x} Chemistry

\begin{tikzpicture}[node distance=2cm]
  
  \node[shape=circle,fill=red] (no) {NO};
  \node[shape=circle,fill=red] (no2) [right of=no] {NO\textsubscript{2}};
  \node[shape=circle,fill=red] (no3) [below of=no2] {NO\textsubscript{3}};
  \node[shape=circle,fill=red] (n2o5) [right of=no2] {N\textsubscript{2}O\textsubscript{5}};

  \draw[->,>=latex,black] (no) -- (no2) node[midway, above] {$O\textsubscript{3}$};
  \draw[->,>=latex,black] (no2) -- (n2o5) node[midway, above] {$O\textsubscript{3}$};
  \draw[->,>=latex,black] (no2) -- (no3) node[midway, right] {$O\textsubscript{3}$};

\end{tikzpicture}
Diurnal Variation of NO$_2$: Measurement from High-Altitude Balloon
Nitric Acid as a Reservoir for $\text{NO}_x$

\[ \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \]
\[ \text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3 \]
\[ \text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O} \]
\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]

$\tau \sim 1-2 \text{ weeks}$

\[ \text{net: } \text{OH} + \text{OH} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_3 \]

Atmospheric Chemistry Lecture 7
Steady-State Continuity Equation Including Loss Due to $O_x$, $NO_x$, and $HO_x$

$$P_{O_x} = \kappa \cdot [O_3] + \alpha \cdot [ON] \cdot [O_3] + \beta \cdot [HO_x] \cdot [O_3]$$

**Solve for $[O_3]$**

$$[O_3] = \frac{P_{O_x}}{\kappa + \alpha \cdot [ON] + \beta \cdot [HO_x]}$$

**Take derivative of $[O_3]$ with respect to $[ON]$**

$$\frac{\partial [O_3]}{\partial [ON]} = \frac{-\alpha \cdot P_{O_x}}{(\kappa + \alpha \cdot [ON] + \beta \cdot [HO_x])^2}$$
Sensitivity of Ozone to Odd Nitrogen Change

\[ S(O_3 | ON) = \frac{\partial [O_3]/[O_3]}{\partial [ON]/[ON]} = \frac{-\alpha \cdot [ON]}{\kappa + \alpha \cdot [ON] + \beta \cdot [HO_x]} \]

\[ \frac{\partial [O_3]/[O_3]}{\partial [ON]/[ON]} = -\frac{l_{NO_x}}{l_{tot}} \]

*For small perturbations, the fractional change in ozone for a given fractional change in odd nitrogen (or NO\textsubscript{x}) is equal to the fraction of the baseline loss that is due to NO\textsubscript{x}.*
Loss Rates due to Catalytic Cycles

Approximate Altitude (km)

Loss Rate Due to Each Cycle ($10^6$ cm$^{-3}$ sec$^{-1}$)

Fraction Loss Due to Cycle (%)