Importance of Radicals (Lectures 9 & 10)

• With a few exceptions, the only reactions between molecules that proceed at appreciable rates are those involving at least one radical

• Radicals require significant energy to form: a bond must be broken

• Radical formation is tied to absorption of photons that “photodissociate” a compound, leading to radical formation

Initiation

\[ \text{O}_2 + \text{photon} \rightarrow \text{O} + \text{O} \]

Propagation

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]
\[ \text{O}_3 + \text{photon} \rightarrow \text{O}(^1\text{D}) + \text{O}_2 \]
\[ \text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} \]
\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]
\[ \text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \]

Termination

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]
Atmospheric Radiation

- Solar irradiance (downwelling) at top of atmosphere occurs at wavelengths between ~200 and 2000 nm (~5750 K “black body” temperature)

Panel (a): Curves of black-body energy versus wavelength for 5750 K (Sun’s approximate temperature) and for 245 K (Earth’s mean temperature). The curves are drawn with equal area since, integrated over the entire Earth at the top of the atmosphere, the solar (downwelling) and terrestrial (upwelling) fluxes must be equal.

Panel (b): absorption by atmospheric gases for a clear vertical column of the atmosphere (1.0 represents complete absorption).

From Houghton, Physics of Atmospheres, 1991

- Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration) of molecules

From Brasseur & Solomon, Aeronomy of the Middle Atmosphere, 1986

- O₂ can not dissociate longward of ~250 nm
- All absorption shown above is dissociative (e.g., leads to production of two O atoms)
- Structure in the O₂ cross section is related to whether the initial transition involves an unbound electronic state (smooth) or involves a specific vibrational level of an electronic state (banded, due to requirement of specific quanta of energy)
Optical Depth of O₂ Absorption

Recall the Beer-Lambert Law:

\[ F(z,\lambda) = F_{\text{TOA}}(\lambda) e^{-\tau(z,\lambda)} \quad (\text{TOA : Top of Atmosphere)} \]

where:

\[ \tau(z,\lambda) = m \int_{z}^{\infty} \sigma_{\lambda}[C] \, dz' \quad (\tau: \text{optical depth}) \]

Also:

\[ \int_{0}^{\infty} [O_2] \, dz' = 4 \times 10^{24} \text{ molecules/cm}^2 \]

<table>
<thead>
<tr>
<th>O₂ Optical Depth for θ = 0°, z = 0 km</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{\text{max}} ) (cm²)</td>
</tr>
<tr>
<td>Schumann-Runge Continuum</td>
</tr>
<tr>
<td>Schumann-Runge Bands</td>
</tr>
<tr>
<td>Herzberg Continuum</td>
</tr>
</tbody>
</table>

Optical Depth of O₃ Absorption

A typical mid-latitude column abundance for O₃ is 300 Dobson units (DU):

\[ 1 \text{ DU} = 2.687 \times 10^{16} \text{ molecules/cm}^2; \quad 300 \text{ DU} = 8 \times 10^{18} \text{ molecules/cm}^2 \]

Aside:

\[ \frac{\text{Column O₃}}{\text{Column Air}} = \frac{8 \times 10^{18}}{2 \times 10^{25}} = 0.4 \text{ parts per million} \Rightarrow \text{Ozone is a trace species!} \]

<table>
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<th>O₃ Optical Depth for θ = 0°, z = 0 km</th>
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<tbody>
<tr>
<td>( \sigma_{\text{max}} ) (cm²)</td>
</tr>
<tr>
<td>Hartley (≈220 to 280 nm)</td>
</tr>
<tr>
<td>Huggins (≈310 to 330 nm)</td>
</tr>
<tr>
<td>Chappuis (≈500 to 700 nm)</td>
</tr>
</tbody>
</table>
Optical Depth of O₃ Absorption

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Aside:

\[ \frac{\text{Column O}_3}{\text{Column Air}} = \frac{8 \times 10^{18}}{2 \times 10^{25}} = 0.4 \text{ parts per million} \Rightarrow \text{Ozone is a trace species!} \]

<table>
<thead>
<tr>
<th>O₃ Optical Depth for ( \theta = 0^\circ, z = 0 \text{ km} )</th>
<th>O₃ Column, ( \tau = 1.0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hartley (~220 to 280 nm)</td>
<td>( \sigma_{\text{max}} \text{ (cm}^2)</td>
</tr>
<tr>
<td></td>
<td>10⁻¹⁷</td>
</tr>
<tr>
<td>Huggins (~310 to 330 nm)</td>
<td>10⁻¹⁹</td>
</tr>
<tr>
<td>Chappuis (~500 to 700 nm)</td>
<td>3 \times 10⁻²¹</td>
</tr>
</tbody>
</table>

Optically Thin!

Solar Spectral Actinic Flux


Photolysis Frequency

For a specific spectral interval, the photolysis frequency (partial $J$ value) of a gas is given by the product of its absorption cross section and the solar irradiance:

$$J_{\text{gas}}(z,\lambda) = \text{Quantum}_\text{Yield}(\lambda) \sigma_{\text{gas}}(\lambda, T) F(z,\lambda)$$

Units: $s^{-1}$ $nm^{-1}$

The total photolysis frequency ($J$ value) is found by integrating $J_{\text{gas}}(z,\lambda)$ over all wavelengths for which the gas photodissociates:

$$J_{\text{gas}}(Z) = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} J_{\text{gas}}(z,\lambda) \, d\lambda$$

Units: $s^{-1}$

Rate of Reaction $= \frac{d[O_3]}{dt} = J [O_3]$; Units of $J$ are $s^{-1}$

More precisely, calculations of photolysis frequencies consider the “spectral actinic flux”, which represents the amount of available photons integrated over all angles, rather than “solar irradiance”. These two quantities differ because of scattering of solar radiation by gases and aerosols, and reflection of radiation by clouds and the surface.
**Bimolecular Gas Phase Reactions**

\[
\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}
\]

\[
\Delta \text{Enthalpy} = -13.8 \text{ kcal/mole}
\]

Exothermic!

Rate of Reaction:
\[
\frac{d\text{CH}_4}{dt} = k [\text{OH}][\text{CH}_4]
\]

Arrhenius Expression for rate constant:
\[
k = 2.45 \times 10^{-12} \times e^{-1775/T} \text{ cm}^3 \text{ sec}^{-1}
\]
Tropospheric Ozone Production versus NO

As NO\textsubscript{x} rises:
[HO\textsubscript{2}] falls faster than [NO] rises,
leading to a decrease in the value of the product of k [NO] [HO\textsubscript{2}],
and hence the production rate of O\textsubscript{3}.

Illustrative calculation of the dependence of O\textsubscript{3} production on [NO]

This curve has key policy implications!

Tropospheric Ozone Production versus NO\textsubscript{x} and VOCs

Ridge: local maximum for O\textsubscript{3} that separates the NOx-limited regime from and VOC limited regime

An important discovery in the past decade is that the focus on hydrocarbon emission controls to combat O\textsubscript{3} pollution may have been partly misdirected. Measurements and model calculations now show that O\textsubscript{3} production over most of the United States is primarily NO\textsubscript{x} limited, not hydrocarbon limited. The early models were in error in part because they underestimated emissions of hydrocarbons from automobiles, and in part because they did not account for natural emission of biogenic hydrocarbons from trees and crops.

Jacob, Chapter 12, Introduction to Atmospheric Chemistry, 1999

Figure: [http://www-personal.umich.edu/~sillman/ozone.htm](http://www-personal.umich.edu/~sillman/ozone.htm)
Day-to-day meteorology (weather!) affects severity and duration of pollution episodes

Maryland has worst air quality during a particular time of year when a certain air circulation system develops

Significant Improvements in **Local** Air Quality since early 1980s
Stratospheric Ozone: Chapman Chemistry

• Production of O₃ initiated when O₂ is photodissociated by UV sunlight

• O₃ formed when resulting O atom reacts with O₂:

\[
\begin{align*}
\text{hv} + \text{O}_2 & \rightarrow \text{O} + \text{O} \quad (1) \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad (2)
\end{align*}
\]

• O₃ removed by photodissociation (UV sunlight) or by reaction with O:

\[
\begin{align*}
\text{hv} + \text{O}_3 & \rightarrow \text{O} + \text{O}_2 \quad (3) \\
\text{O} + \text{O}_3 & \rightarrow \text{O}_2 + \text{O}_2 \quad (4)
\end{align*}
\]

This reaction sequence was first worked out in the 1930s by Sidney Chapman, an English mathematician and geophysicist.

Chapman Chemistry

• The cycling between O and O₂ (rxns 2 and 3) occurs much more rapidly than leakage into (rxn 1) or out of the system (rxn 4)

• The sum O + O₃ is commonly called “odd oxygen”

Rxn (1) produces two odd oxygen molecules
Rxn (4) consumes two odd oxygen molecules
and reactions 2 and 3 recycle odd oxygen molecules
Calculated fraction of odd oxygen loss due to various families of radicals

After Osterman et al., GRL, 24, 1107, 1997;
Sen et al., JGR, 103, 3571, 1998;
Sen et al., JGR, 104, 26653, 1999.

One Atmosphere – One Photochemistry

**Stratosphere**

- HO₂ formation:
  \[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]
- HO₂ loss:
  \[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \]
- Net:
  \[ \text{O}_3 + \text{O}_3 \rightarrow 3\text{O}_2 \]

**Troposphere**

- HO₂ formation:
  \[ \text{OH} + \text{CO} \rightarrow \text{HO}_2 + \text{CO}_2 \]
- HO₂ loss:
  \[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]
  Followed by:
  \[ \text{NO}_2 \text{hv} \rightarrow \text{NO} + \text{O} \]
  \[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]
- Net:
  \[ \text{CO} + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{O}_3 \]

Above Tropopause:
- Lots of O₃, little CO

Below Tropopause:
- Lots of CO, little O₃

Courtesy of Laura Pan, NCAR
Total Organic Chlorine (CCl\textsubscript{y}):
- Peaked at ~3.6 ppb around 1993
- Slowly declining
- Montreal Protocol and Amendments have banned production of CFCs

CFCs:
- long lived (50 to 100 yr lifetime)
- decompose in the stratosphere
- lose memory of emission location when enter stratosphere

Chlorine Abundance, Mid-Latitude Stratosphere

Note: Below ~30 km, ClO << CINO\textsubscript{3} and HCl

Zander \textit{et al.}, GRL, 1996
Chlorine Source Gases

Primary Sources of Chlorine for the Stratosphere in 1999

Table Q7-1. Atmospheric Lifetimes and Ozone Depletion Potentials of some halogen source & HFC substitute gases.

<table>
<thead>
<tr>
<th>Gas Description</th>
<th>Atmospheric Lifetime (years)</th>
<th>Ozone Depletion Potential (ODP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine gases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFC-11</td>
<td>45</td>
<td>1</td>
</tr>
<tr>
<td>CFC-12</td>
<td>100</td>
<td>0.02</td>
</tr>
<tr>
<td>CFC-113</td>
<td>85</td>
<td>0.05</td>
</tr>
<tr>
<td>Carbon tetrachloride (CCl4)</td>
<td>26</td>
<td>0.82</td>
</tr>
<tr>
<td>HFCF2</td>
<td>1-17</td>
<td>0.01-0.12</td>
</tr>
<tr>
<td>Methyl chloroform(CHCl3)</td>
<td>3</td>
<td>0.16</td>
</tr>
<tr>
<td>Methyl chloride (CH3Cl)</td>
<td>1</td>
<td>0.02</td>
</tr>
<tr>
<td>Bromine gases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halon-1301</td>
<td>65</td>
<td>15.0</td>
</tr>
<tr>
<td>Halon-1211</td>
<td>16</td>
<td>7.9</td>
</tr>
<tr>
<td>Methyl bromide (CH3Br)</td>
<td>0.8</td>
<td>0.05</td>
</tr>
<tr>
<td>Very short-lived gases (e.g., CHBr3)</td>
<td>Less than 0.5</td>
<td>Very low</td>
</tr>
<tr>
<td>Hydrofluorocarbons (HFCs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HFC-134a</td>
<td>13.4</td>
<td>0</td>
</tr>
<tr>
<td>HFC-13</td>
<td>222</td>
<td>0</td>
</tr>
</tbody>
</table>

Bromine Source Gases

Halons:
- fire extinguishing agents
- production in developed world halted by Montreal Protocol
- present emissions primarily from "banks"

CH3Br:
- fumigant; released by biomass burning
- production halted by Montreal Protocol
- significant natural & human sources

VSL Gases (e.g., CHBr3, CH2Br2):
- emitted mainly by ocean biology
- not considered in most ozone calcs
- chemistry of decomposition products subject of active research
Ozone Depletion at Mid-Latitudes

Ozone data from http://www.bodekerscientific.com/data/ozone

\[
\text{Column Ozone Anomaly (DU)} = 20.5 \text{ DU} + 3.89 \text{ DU / W m}^{-2} \times \text{TSI} + (-11.5 \text{ DU / ppb} \times \text{Halogens}) + (-11.4 \text{ DU / SOD \times Strat} \tau) + (-1.27 \text{ DU / m s}^{-1} \times \text{QBO Index})
\]

where SSA = Sulfate Surface Area

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Ozone responds to:
- a) rise and fall of chlorine
- b) volcanic perturbations to aerosol loading
- c) amount of bromine in lowermost stratosphere

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Heterogeneous Chemistry, Mid-Latitude vs Polar Regions

In all cases, $\gamma$ must be measured in the laboratory.

Reaction probabilities given for various surface types, with formulations of various degrees of complexity, in Section 5 of the JPL Data Evaluation.

Atmospheric Chemistry and Physics by Seinfeld and Pandis provides extensive treatment of aqueous phase chemistry, properties of atmospheric aerosol, organic aerosols, etc.

Polar Ozone Loss

- Cold Temperatures $\rightarrow$ Polar Stratospheric Clouds (PSCs)
- Reactions on PSC surfaces lead to elevated ClO
  
  \[ \text{HCl} + \text{CINO}_3 \rightarrow \text{Cl}_2 \text{ (gas)} + \text{HNO}_3 \text{ (solid)} \]
  
  \[ \text{CINO}_3 + \text{H}_2\text{O} \rightarrow \text{HOCI} + \text{HNO}_3 \]
  
  \[ \text{Cl}_2 + \text{SUNLIGHT} + \text{O}_3 \rightarrow \text{CIO} \]
  
  \[ \text{HOCI} + \text{SUNLIGHT} + \text{O}_3 \rightarrow \text{CIO} \]
  
  \[ \text{HNO}_3 \text{ SEDIMENTS (PSCs fall due to gravity)} \]

- Elevated ClO + Sunlight destroys O$_3$
- BrO : Reaction Partner For ClO $\Rightarrow$ Additional O$_3$ Loss
Arctic Ozone 2011 in Context of Prior Years

Future Mid-Latitude Ozone: N$_2$O

Ozone depleting NO$_x$ cycles speed up with increasing N$_2$O throughout the middle stratosphere, where these cycles make the largest relative contribution to odd oxygen loss. As NO$_x$ increases due to rising N$_2$O, the abundance of HO$_2$ and ClO radicals declines, particularly in the lower stratosphere, leading to reduced rates in the total speed of all ozone depleting cycles (red region, Fig 5a).

Fig. 5. (a) N$_2$O-8.5 ozone minus N$_2$O-2.6 ozone in the 2090s decade, calculated as a percentage of ozone in the N$_2$O-2.6 simulation. (b) 2090s-decade N$_2$O-8.5 total column ozone minus N$_2$O-2.6 total column ozone.

Revell et al., ACP, 2012
Rising CH₄ leads to ozone loss in the upper and lower stratosphere by increasing the speed of HOₓ-mediated loss cycles. However, there are other processes that result in more ozone:

- Rising CH₄ leads to more stratospheric H₂O, cooling the this region of the atmosphere, which slows the rate of all ozone loss cycles.
- Rising CH₄ speeds up the rate of Cl+CH₄, shifting chlorine from ClO into HCl
- Rising CH₄ leads to more HO₂ in the lowermost stratosphere, where there is sufficient CO to result in production of O₃ by so-called “photochemical smog chemistry”

Fig. 6. (a) CH₄-8.5 ozone minus CH₄-2.6 ozone in the 2090s decade, calculated as a percentage of ozone in the CH₄-2.6 simulation. (b) 2090s-decade CH₄-8.5 total column ozone minus CH₄-2.6 total column ozone.

Revell et al., ACP, 2012

EXCESS SKIN CANCER CASES IN THE UNITED STATES,
PER YEAR, DUE TO OZONE DEPLETION
FOR VARIOUS CFC EMISSION SCENARIOS


See also Slaper et al., Estimates of ozone depletion and skin cancer incidence to examine the Vienna Convention achievements, Nature, 384, 256–258, 1996, who state:

The no-restrictions and Montreal Protocol scenarios produce a runaway increase in skin cancer incidence, up to a quadrupling and doubling, respectively, by year 2100.
Second Exam

– Thursday, 11 April, 2:00 pm to 3:15 pm
– CSS 2416
– 6 questions (multi-part)
– Closed book, no notes

– Focus almost entirely on Lectures 9 to 17
– Mix of conceptual questions and simple calculations
– Please bring a calculator (we’ll have extras if you forget)
– iPad, iPhone, or any other device able to either go on the web or store notes is not allowed

– Backbone of course is the lectures; questions may draw upon material from the readings *that has been emphasized in lecture*

– We’ll be present: *please let us know if a question requires clarification*
  If so, we’ll announce clarification to entire class 😊

– Exam for 633 will differ somewhat from exam for 433