Review of Lectures 9 to 16
AOSC 433/633 & CHEM 433

Ross Salawitch

• Exam on Thursday:
  Conceptual questions only: no calculators
  Closed book; no notes
• ELMS gradebook should be current
  please let us know of any issues
• Please note:
  Last day to drop a course with a "W" is 12 April
  Students dropping a course on Testudo have until 11pm on 12 April
  Drop/Add services for Spring 2017 will no longer be available after 11pm on 12 April
  Students who need to come in person to drop a course have until 5 pm on 12 April

11 April 2017
Importance of Radicals

• 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

\[
O_2 + \text{photon} \rightarrow O + O
\]

Propagation

\[
O + O_2 + M \rightarrow O_3 + M \\
O_3 + \text{photon} \rightarrow O(^1D) + O_2 \\
O(^1D) + H_2O \rightarrow OH + OH \\
OH + O_3 \rightarrow HO_2 + O_2 \\
HO_2 + O \rightarrow OH + O_2
\]

Termination

\[
HO_2 + HO_2 \rightarrow H_2O_2 + O_2
\]
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).


• Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration) of molecules
Absorption Cross Section of $\text{O}_2$

- $\text{O}_2$ cannot dissociate longward of $\sim 250$ nm
- All absorption shown above is dissociative (e.g., leads to production of two O atoms)
- Structure in the $\text{O}_2$ 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)

From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986
Optical Depth of O₂ Absorption

Recall the Beer-Lambert Law:

\[ F(z, \lambda) = F_{\text{TOA}}(\lambda) e^{-\tau(z, \lambda)} \]

(TOA : Top of Atmosphere)

where:

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

(\( \tau \): optical depth)

Also:

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

<table>
<thead>
<tr>
<th>O₂ Optical Depth for ( \theta = 0^\circ ), ( z = 0 \text{ km} )</th>
<th>( \sigma_{\text{max}} \text{ (cm}^2) )</th>
<th>( \tau \text{ (0 km)} )</th>
<th>( e^{-\tau \text{ (0 km)}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schumann-Runge Continuum</td>
<td>( 10^{-17} )</td>
<td>( 4 \times 10^7 )</td>
<td>0.</td>
</tr>
<tr>
<td>Schumann-Runge Bands</td>
<td>( 10^{-20} )</td>
<td>( 4 \times 10^4 )</td>
<td>0.</td>
</tr>
<tr>
<td></td>
<td>( 3 \times 10^{-23} )</td>
<td>120</td>
<td>( 7.6 \times 10^{-53} )</td>
</tr>
<tr>
<td>Herzberg Continuum</td>
<td>( 10^{-23} )</td>
<td>40</td>
<td>( 4.2 \times 10^{-18} )</td>
</tr>
</tbody>
</table>
Optical Depth of $O_3$ Absorption

A typical mid-latitude column abundance for $O_3$ 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:

$$\frac{\text{Column } O_3}{\text{Column Air}} = \frac{8 \times 10^{18}}{2 \times 10^{25}} = 0.4 \text{ parts per million} \Rightarrow \text{Ozone is a trace species!}$$

<table>
<thead>
<tr>
<th>$O_3$ Optical Depth for $\theta = 0^\circ$, $z = 0$ km</th>
<th>$\sigma_{\text{max}}$ (cm$^2$)</th>
<th>$\tau$ (0 km)</th>
<th>$e^{-\tau}$ (0 km)</th>
<th>$O_3$ Column, $\tau = 1.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hartley ($\sim$220 to 280 nm)</td>
<td>$10^{-17}$</td>
<td>80</td>
<td>$1.8 \times 10^{-35}$</td>
<td>3.7 DU</td>
</tr>
<tr>
<td>Huggins ($\sim$310 to 330 nm)</td>
<td>$10^{-19}$</td>
<td>0.8</td>
<td>0.45</td>
<td>372 DU</td>
</tr>
<tr>
<td>Chappuis ($\sim$500 to 700 nm)</td>
<td>$3 \times 10^{-21}$</td>
<td>0.024</td>
<td>~1.0</td>
<td>12,400 DU</td>
</tr>
</tbody>
</table>
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:

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

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 $= \frac{dO_3}{dt} = J \ [O_3]$; 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.
NO$_2$ Photolysis

![Graphs showing NO$_2$ Photolysis](image)
$O_3 \rightarrow O^{(1D)}$ Photolysis

![Diagram showing $O_3 \rightarrow O^{(1D)}$ Photolysis with various plots and graphs illustrating quantum yield, altitude, solar zenith angle, and wavelength distributions.]

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Bimolecular Gas Phase Reactions

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

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

Rate of Reaction

\[ \frac{d[\text{CH}_4]}{dt} = k [\text{OH}][\text{CH}_4] \]

Arrhenius Expression for rate constant:

\[ k = 2.45 \times 10^{-12} \times e^{-1775/T} \text{ cm}^3 \text{ sec}^{-1} \]

\[ \frac{E_A}{R} \Rightarrow \text{Activation Energy / Gas Constant} \]

\[ R = 8.3143 \times 10^7 \text{ erg} / (\text{K mole}) = 2.87 \times 10^6 \text{ erg} / (\text{K gm}) \text{ for air} \]

\[ k_c e^{\Delta S / R} \]

\[ \text{Entropy Term} \]

\[ \text{A factor} \]

\[ \text{Energy Term} \]

Figure 3.3 Barrier energies for the forward reaction \( E_a \) and the reverse reaction \( E_a + \Delta H \).

Tropospheric Ozone Production versus NO

Production of Tropospheric O₃ limited by: ____________ ?

As NOₓ rises:

[HO₂] falls faster than [NO] rises,
leading to a decrease in the value ______________

Illustrative calculation of the dependence of O₃ 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 NO\textsubscript{x}-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

http://www.mde.state.md.us/assets/document/BJH%20-%20Basics%20on%20Ozone%20Transport.ppt
Dramatic Improvements Local Air Quality, Past 4 Decades

Days Exceeding 2015 EPA Std (8 hr $O_3 > 70$ ppb)

Maryland Dept of the Environment

Days BWI $T_{MAX} > 90^\circ$ F

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NO$_2$ Trends from Space

Krotkov et al., ACP, 2016
SO₂ Trends from Space

Krotkov et al., ACP, 2016
Sulfate Deposition

1994

Sulfate ion concentration, 1994

2013

Sulfate ion concentration, 2013

http://nadp.sws.uiuc.edu/
pH

1994

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 1994

Sites not pictured:
- Alaska 01
- Alaska 03
- Puerto Rico 20

2013

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2013

Sites not pictured:
- Alaska 01
- Alaska 02
- Alaska 03
- Alaska 97
- Puerto Rico 20
- British Columbia 22
- Saskatchewan 21

http://nadp.sws.uiuc.edu/
Stratospheric Ozone: Chapman Chemistry

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

• O₃ formed when resulting O atom reacts with O₂:

\[ \text{hv} + \text{O}_2 \rightarrow \text{O} + \text{O} \quad (1) \]
\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (2) \]

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

\[ \text{hv} + \text{O}_3 \rightarrow \text{O} + \text{O}_2 \quad (3) \]
\[ \text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 \quad (4) \]

This reaction sequence was first worked out in the 1930s by Sidney Chapman, an English mathematician and geophysicist.
• The cycling between O and O\textsubscript{2} (rxns 2 and 3) occurs \textit{much} more rapidly than leakage into (rxn 1) or out of the system (rxn 4)

• The sum O + O\textsubscript{3} is commonly called “\textit{odd oxygen}”

Rxn (1) produces two \textit{odd oxygen} molecules
Rxn (4) consumes two \textit{odd oxygen} molecules

and reactions 2 and 3 recycle \textit{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**

HO$_2$ formation:

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]

HO$_2$ 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**

HO$_2$ formation:

\[ \text{OH} + \text{CO} \rightarrow \text{HO}_2 + \text{CO}_2 \]

HO$_2$ 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 O$_3$, little CO

Below Tropopause:

Lots of CO, little O$_3$

Courtesy of Laura Pan, NCAR
Tropospheric Chlorine Loading

Total Organic Chlorine ($\text{CCl}_y$):
- 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

Table 5A-2, WMO/UNEP (2014)
Chlorine Abundance, Mid-Latitude Stratosphere

Zander et al., GRL, 1996

Note: Below ~30 km, ClO << CINO₃ and HCl
Chlorine Source Gases

Primary Sources of Chlorine for the Stratosphere in 1999

Chlorine source gases

- **Other gases**
- **Methyl chloroform** (CH$_3$CCl$_3$)
- **HCFCs** (e.g., HCFC-22 = CHClF$_2$)
- **CFC-113** (CCl$_2$FCClF$_2$)
- **Carbon tetrachloride** (CCl$_4$)
- **CFC-11** (CCl$_3$F)
- **CFC-12** (CCl$_2$F$_2$)
- **Methyl chloride** (CH$_3$Cl)

![Bar chart showing the sources and amounts of chlorine gases](chart.png)

| Table Q7-1. Atmospheric Lifetimes and Ozone Depletion Potentials of some halogen source & HFC substitute gases. |
| --- | --- | --- |
| **Gas** | Atmospheric Lifetime (years) | Ozone Depletion Potential (ODP) |
| **Halogen source gases** |  |
| Chlorine gases |  |
| CFC-11 | 45 | 1 |
| CFC-12 | 100 | 0.82 |
| CFC-113 | 85 | 0.85 |
| Carbon tetrachloride (CCl$_4$) | 26 | 0.82 |
| HCFCs | 1–17 | 0.01–0.12 |
| Methyl chloroform (CH$_3$CCl$_3$) | 5 | 0.16 |
| Methyl chloride (CH$_3$Cl) | 1 | 0.02 |
| Bromine gases |  |
| Halon-1301 | 65 | 15.9 |
| Halon-1211 | 16 | 7.9 |
| Methyl bromide (CH$_3$Br) | 0.8 | 0.66 |
| Very short-lived gases (e.g., CHBr$_3$) | Less than 0.5 | b very low |
| Hydrofluorocarbons (HFCs) |  |
| HFC-134a | 13.4 | 0 |
| HFC-23 | 222 | 0 |
Bromine Source Gases

**Halon-1301** (CBrF₃):
- fire extinguishing agents
- production halted by Montreal Protocol
- present emissions primarily from “banks”

**Halon-1211** (CBrClF₂):
- fumigant; released by biomass burning
- production halted by Montreal Protocol
- significant natural & human sources

**Methyl bromide** (CH₃Br):
- emitted mainly by ocean biology
- not considered in most ozone calcs
- chemistry of decomposition products subject of active research

**Very-short lived gases** (e.g., bromoform = CHBr₃):
- 15%

**Other halons**:
- 4%

**Natural sources**:
- 27-42%

**Human-made sources**:
- 5-20%
- 14%
- 20%

Total bromine amount (parts per trillion)
Ozone Depletion at Mid-Latitudes

Column Ozone Anomaly (DU) =

\[
19.6 \text{ DU} + 2.38 \text{ DU}/\text{W m}^{-2} \times \text{TSI} - 12.4 \text{ DU}/\text{ppb} \times \text{Halogens} - 0.87 \text{ DU} \times \ln (\text{SSA}) - 0.02 \text{ DU}/\text{m s}^{-1} \times \text{QBO}
\]

where

- TSI = total solar irradiance
- Halogens = stratospheric chlorine & bromine loading
- SSA = Sulfate Surface Area
- QBO = Quasi-biennial oscillation of the direction of winds in the tropical lower strat

Ozone data from
http://acdb-ext.gsfc.nasa.gov/Data_services/merged
BrO$_x$ : BrO and Br

BrO is central to stratospheric photochemistry, at mid-latitudes and polar regions

**Production:**

- $\text{CH}_3\text{Br} + h\nu \rightarrow \text{Inorganic bromine}$
- Halons $+ h\nu \rightarrow \text{Inorganic bromine}$
- $\text{CHBr}_3 + h\nu \rightarrow \text{Inorganic bromine}$
- $\text{CH}_2\text{Br}_2 + h\nu \rightarrow \text{Inorganic bromine}$

\{ Considered in global models \}
\{ Generally neglected in global models \}

**Final sink:** HBr solubility & rainout (lowermost stratosphere)
BrO\textsubscript{x} : BrO and Br

BrO is central to \textit{stratospheric} photochemistry, at mid-latitudes and polar regions:

Rapid inner cycle:

BrO formation:

\[
\text{BrO formation: } \quad \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \quad (1)
\]

BrO loss:

\[
\begin{align*}
\text{BrO loss: } & \quad \text{BrO} + \text{NO} \rightarrow \text{Br} + \text{NO}_2 \quad (2) \\
& \quad \text{or} \quad \text{BrO} + \text{O} \rightarrow \text{Br} + \text{O}_2 \quad (3) \\
& \quad \text{or} \quad \text{BrO} + \text{ClO} \rightarrow \text{BrCl} + \text{O}_2 \quad (4a) \\
& \quad \quad \rightarrow \text{ClOO} + \text{Br} \quad (4b) \\
& \quad \quad \rightarrow \text{OClO} + \text{Br} \quad (4c)
\end{align*}
\]

Can show:

\[
\frac{d\text{O}_3}{dt} + \frac{d\text{O}}{dt} = \frac{d(\text{Odd Oxygen})}{dt} = -2k_3[\text{BrO}][\text{O}]
\]

As a convenient short hand, \textit{we consider BrO to be odd oxygen}
Bromine Overview

Bromine is more efficient, per molecule, than chlorine at removing ozone because:

• Organic bromine compounds degrade faster than CFCs
  – lifetime of CH₃Br much shorter than lifetime of CFCs
  – Therefore Brₓ liberated more easily from CBrₓ than Clₓ liberated from CClₓ

• BrO/Brₓ >> ClO/Clₓ
  
  \[
  \text{Br} + \text{CH}_{4} \rightarrow \text{HBr} + \text{CH}_{3} \text{ is endothermic and has rate constant of zero}
  \]
  
  \[
  \text{Cl} + \text{CH}_{4} \rightarrow \text{HCl} + \text{CH}_{3} \text{ is exothermic and proceeds at reasonable rate}
  \]
  
  Also, \( J_{\text{BrONO}_2} > J_{\text{ClONO}_2} \)

• Loss due to BrO+ClO reaction generally counted as “bromine loss”,
  even though loss of ozone by this cycle depends on Brₓ and Clₓ
Ozone responds to:

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

Salawitch et al., GRL, 2004
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 → Polar Stratospheric Clouds (PSCs)**
- **Reactions on PSC surfaces lead to elevated ClO**
  
  HCl + CINO₃ → Cl₂ (gas) + HNO₃ (solid)
  CINO₃ + H₂O → HOCl + HNO₃
  Cl₂ + SUNLIGHT + O₃ → ClO
  HOCl + SUNLIGHT + O₃ → ClO
  HNO₃ SEDIMENTS (PSCs fall due to gravity)

- **Elevated ClO + Sunlight destroys O₃**
- **BrO: Reaction Partner for ClO → Additional O₃ Loss**
EP/TOMS Total Ozone for Sep 1, 2001

Dobson Units

Dark Gray < 100, Red > 500 DU
Arctic Ozone 2011 in Context of Prior Years

The graph shows the ozone loss (DU) based on average vortex size over various years from 1970 to 2010. The data points are color-coded by year, with each year represented by a different color scale. The vertical bars indicate the variability within each year. The graph also includes a trend line showing the increase in ozone loss over the years.
If the stratosphere continues to cool, for which region of the stratosphere will ozone be most vulnerable to future decline?

Figure 4–11, WMO/UNEP (2011)
Arctic Temperature: Mar 2011

Arctic Temperature: Mar 2015

Arctic Temperature: Mar 2017

http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/50mbnhlo.png

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, 13 April, 2:00 pm to 3:15 pm
– CSS 2416
– Closed book, no notes

– Focus mainly on Lectures 9 to 16
– Conceptual questions only: no calculator
– Backbone of course is the lectures and material from readings highlighted in class
– We’ll be present: please let us know if a question requires clarification
– Exam for 633 will differ somewhat from exam for 433