Stratospheric Chemistry – Part 2
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- Quick summary from last time
- The controversy
- The “Big Surprise of 1985”
- Heterogeneous chemistry
- Chlorine and NOy
- Why Antarctica and the Arctic?
- The story continues

Odd oxygen

\[
\begin{align*}
O & \xrightarrow{hv} O_3 \\
O_2 & \xrightarrow{hv} O \\
O + catalysts & \xrightarrow{hv} O_2 \\
O_2 & \xrightarrow{hv} O
\end{align*}
\]
Chapman chemistry (in steady state)

Slow and exactly balance

\[ J_{O_2}[O_2] = k_4[O][O_3] \]

\[ [O][O_3] = \frac{J_{O_2}}{k_4} [O_2] \]

\[ [O_3] \approx 0.21 \left( \frac{k_2}{k_4} \right)^{1/2} \left( \frac{J_{O_2}}{J_{O_1}} \right)^{1/2} \left[ M \right]^{3/2} \]

Fast and approx. balance

\[ k_1[O_2][M] \approx J_{O_1}[O_1] \]

Catalysts

\[ X + O_3 \rightarrow XO + O_2 \]
\[ XO + O \rightarrow X + O_2 \]
\[ O_3 + O \rightarrow O_2 + O_2 \]

\[ N_2O + O(^1D) \rightarrow NO + NO \text{ (about 4% of all N}_2O \text{ oxidation)} \]
\[ H_2O + O(^1D) \rightarrow OH + OH \]
\[ CF_xCl_y + hv \rightarrow + O_2 \rightarrow + hv \ldots \rightarrow CO_2 + xF + yCl \]

SSTs – H_2O, NO_x
Chlorine – volcanoes, space shuttle
N_2O from fertilizing
H_2O from CH_4 oxidation
CFCs – refrigerants, propellants, foam blowing, etc.
“...are unusually stable chemically and only slightly soluble in water and might therefore persist and accumulate in the atmosphere ... The presence of these compounds constitutes no conceivable hazard.” (Lovelock)

Must have reasonably long lifetimes in troposphere (~years or more)

- Can’t be too soluble in water (e.g. HCl, NaCl)
- Can’t react rapidly with OH or O₃
- Can’t have large cross sections at visible λs

- Examples
  N₂O – hundreds of years
  F-11 (CFCl₃) – 50 years
  F-12 (CF₂Cl₂) – 100 years
  HCFCs (CHFCl₂) – year
  CH₃Br – ~1-2 years

The pieces come together!

“spark”

CFCl₃ + hv → CFCl₂ + Cl
CF₂Cl₂ + hv → CF₂Cl + Cl

release

Cl + O₃ → ClO + O₂
ClO + O → Cl + O₂

“flame”

Net - O₃ + O → O₂ + O₂

transport

O₂ + hv → O + O
O + O₂ + M → O₃ + M
O₃ + hv → O₂ + O
O₂ + O → O₂ + O₂

‘un’reactivity

source
Which one is it?
The SST story evolves…

SSTs make ozone (smog chemistry)

SSTs destroy ozone

Those darned lab chemists

Meanwhile, scientists refine their understanding

But Industry is ready, and they come our firing!

CFCs are heavier than air, and don’t rise to the stratosphere – they sink!

There is more chlorine in sea spray than from CFCs!

Chlorine may get to the stratosphere, but it doesn’t form ClO!

The natural variability of ozone is greater than any change expected due to man-made chemicals!

Even if there is ozone loss, there is no proof that more ultraviolet light will reach the surface!
What really goes on?

\[
\begin{align*}
\text{Couples } \text{ClO}_x \text{ to } \text{NO}_x &:
\begin{align*}
\text{Cl} + \text{O}_3 &\rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{O} &\rightarrow \text{Cl} + \text{O}_2 \\
\text{ClO} + \text{NO} &\rightarrow \text{Cl} + \text{NO}_2 \\
\text{ClO} + \text{NO}_2 + \text{M} &\rightarrow \text{ClNO}_3 \\
\text{ClNO}_3 + \text{hv} &\rightarrow \text{Cl} + \text{NO}_3 \\
&\quad \rightarrow \text{ClO} + \text{NO}_2
\end{align*}
\]
\]
\[
\begin{align*}
\text{Cl} + \text{HO}_2 &\rightarrow \text{HCl} + \text{O}_2 \\
\text{Cl} + \text{CH}_4 &\rightarrow \text{HCl} + \text{CH}_3 \\
\text{ClO} + \text{OH} &\rightarrow \text{HCl} + \text{CH}_3 \\
&\quad \rightarrow \text{Cl} + \text{HO}_2 \\
\text{HCl} + \text{OH} &\rightarrow \text{H}_2\text{O} + \text{Cl} \\
\text{ClO} + \text{HO}_2 &\rightarrow \text{HOCl} + \text{O}_2 \\
\text{HOCl} + \text{hv} &\rightarrow \text{Cl} + \text{OH}
\end{align*}
\]
\]

And NO\textsubscript{x} is coupled to HO\textsubscript{x}!

\[
\begin{align*}
\text{OH} + \text{O}_3 &\rightarrow \text{HO}_2 + \text{O}_2 \\
\text{OH} + \text{O} &\rightarrow \text{O}_2 + \text{H} \\
\text{OH} + \text{CO} &\rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} &\rightarrow \text{HO}_2 + \text{M} \\
\text{HO}_2 + \text{O} &\rightarrow \text{OH} + \text{O}_2 \\
\text{HO}_2 + \text{O}_3 &\rightarrow \text{OH} + 2\text{O}_2 \\
\text{OH} + \text{HO}_2 &\rightarrow \text{H}_2\text{O} + \text{O}_2 \\
\text{HO}_2 + \text{HO}_2 &\rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{HO}_2 + \text{NO} &\rightarrow \text{NO}_2 + \text{OH} \\
\text{OH} + \text{NO}_2 + \text{M} &\rightarrow \text{HNO}_3 + \text{M} \\
\text{HNO}_3 + \text{OH} &\rightarrow \text{H}_2\text{O} + \text{NO}_3 \\
\text{HNO}_3 + \text{hv} &\rightarrow \text{OH} + \text{NO}_2 \\
\text{HO}_2 + \text{NO}_2 &\rightarrow \text{HO}_2\text{NO}_2 + \text{M} \\
\text{HO}_2\text{NO}_2 + \text{hv} &\rightarrow \text{OH} + \text{NO}_3
\end{align*}
\]
\]

\[\text{+ halogen reactions...}\]
Which reactions determine the rate of ozone loss?

ClO + NO → Cl + NO₂
NO₂ + hν → NO + O
O + O₃ + M → O₂ + M

Net: ClO + O₂ → Cl + O₃

this step reforms ozone nearly as fast as it is destroyed by chlorine atoms!

\[-\frac{d([O₃]+[O])}{dt} = (k_{O_3}[Cl][O₃] - k_{NO}[ClO][NO]) + k_{O}[ClO][O]\]

Assume steady state

\[-k_{O_3}[Cl][O₃] + k_{O}[ClO][O]\]

\[-\frac{d([O₃]+[O])}{dt} = 2k_{O}[ClO][O]\]

“twice the rate-determining step”

Build a “model”

1. Source gas
2. Release of radical
3. Fast cycling/partitioning
4. Rate determining step
5. Short-lived reservoirs
6. Long-lived reservoirs
7. Removal
Summary of important points

• Stratospheric ozone is produced by photolysis of $O_2$, a process that is governed by abundances of $O_2$ and UV output of the sun. Mankind can’t easily tamper with these parameters.

• Sir Sydney Chapman (who spent a lot of time in Boulder) nearly got it right. He was able to account for ozone in the stratosphere to within about a factor of two with just four simple reactions. You might as well memorize these… they will reappear on comps and cumulative exams (and it beats what you need to know to get the other factor of two!)

• Gases that are long-lived in the troposphere will eventually reach the stratosphere, where they nearly all break down (‘oxidize’) to produce highly reactive radicals that catalytically destroy ozone. It doesn’t matter where these gases originate from – the troposphere is the great homogenizer. The 1995 Nobel Prizes in Chemistry were awarded to Paul Crutzen, Mario Molina, and Sherry Rowland for recognizing the importance of this concept.

• The radical ‘families’ are highly coupled – changes in abundances of one family will result in changes in the others. Thus, the system is non-linear (although reasonably well behaved). However, it means that you can’t just scale ozone losses with emissions. A ‘simple’ stratospheric model has dozens of chemical species and hundreds of chemical reactions. It will run on a PC (I have one written by Michael Prather on the computer that I am using for this lecture).

• Having a good idea isn’t good enough. It takes a lot of measurements to prove your point – or a global crisis… stay tuned for Part 2!

How Much NO$_x$ is There?

$\text{NO}_x^{\text{strat}} \sim \text{HNO}_3 + \text{N}_2\text{O}_5 + \text{NO} + \text{NO}_2 + \text{NO}_3 + \text{CINO}_3 = 0\text{-}15 \text{ ppb}$

From Ed Dunlea’s lecture

From Michelsen et al., JGR 103, 28347-28359, 1998
Stratospheric chlorine burden

\[ \text{Cl}_2 \sim \text{HCl} + \text{ClNO}_3 + \text{ClO} + \text{HOCl} \]

2-4 ppb

Zander et al., GRL, 23, 2357-2360, 1996

How the radical families contribute to ozone loss

\[ \text{HO}_x (\text{H}_2\text{O}, \text{CH}_4) \]
5-10 ppm

\[ \text{ClO}_x (\text{CFCs}) \]
3 ppb

\[ \text{NO}_x (\text{N}_2\text{O}) \]
10-15 ppb

FIGURE 4.12 Diurnally averaged rates of production and loss of odd oxygen in the upper stratosphere (30-50 km) calculated with a photochemical model for conditions of the ATMOS measurements at 50°N, May 1 (Minchew et al., 1995). Model calculations were constrained by measured profiles for \( O_3 \), \( \text{HO}_x \), and \( \text{CH}_4 \). Photolysis of \( O_3 \) is the only source of odd oxygen. The total predicted removal rate of odd oxygen is given by the solid curve; removal rates for specific catalytic cycles are also shown.
The World Breathes a Sign of Relief…
In the form of CFCs

![Graph showing CFC emissions (1972-1992)]

**FIGURE 12.12** Estimated global annual emissions of CFC-11 and CFC-12 (adapted from World Meteorological Organization, 1995).

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Atmospheric Ozone 1985
The First Big WMO Ozone Assessment

“The formation of ClO₂…may serve as a temporary
ClOₓ reservoir…. The subsequent chemistry of
Cl₂O₂, however, is not well defined. Its likely fate is
photolysis and reaction with Cl, O, or OH. Mutual
reactions between ClO are expected to become
important at ClOₓ levels exceeding 10 ppb.” (Vol 3,
page 38)

“In assessing the current evidence relating to the question
whether or not aerosols perturb the homogeneous chemistry
related to stratospheric ozone, it can be concluded that the
effects are minor and are unlikely to change our overall
picture of the chemistry of the stratosphere.” (Vol 3, page 48)

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The 1994 Assessment
Joseph Farman, head of the Geophysical Unit of the British Antarctic Survey, reports on seasonal ozone depletion over Antarctica, describing a 30 to 40% annual decline in Antarctic ozone. His findings correspond to the loss of ozone.

The Big Surprise of 1985!

FIGURE 12.16: Average total column ozone measured in October at Halley Bay, Antarctica, from 1957 to 1994 (DU = Dobson units). This figure is adapted from Jones and Shanklin (1995).
Three Theories

Solar activity – increased NO\textsubscript{x} at high altitudes would catalyze ozone loss

Dynamical – enhanced vertical lofting of air over Antarctica in springtime, troposphere low in ozone (mixing ratio)

Chlorine – heterogeneous reactions on polar stratospheric clouds convert HCl and ClNO\textsubscript{3} into sources of Cl\textsubscript{O}, rapid catalysis by unknown mechanism

NOZE (1986 National Ozone Experiment)

- Enhanced OC\textsubscript{IO} (indicator of bromine and chlorine chemistry)
- Low N\textsubscript{2}O (not vertical lifting of low-ozone air)

Susan Solomon, Ryan Sanders, Phil Solomon, Robert deZafra, Barney Farmer, Geoff Toon, Dave Hofmann, Jerald Harder
The Smoking Gun!

Ozone and ClO are anticorrelated

**But How?**

**McElroy and Wofsy**

\[
\text{ClO} + \text{BrO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2 \\
\quad \rightarrow \text{OCIO} + \text{Br}
\]

→ Not much Bry

**Solomon et al.**

\[
\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2 \\
\text{HOCl} + \text{hv} \rightarrow \text{OH} + \text{Cl}
\]

→ Slow

**Molina and Molina**

\[
\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M} \\
\text{Cl}_2\text{O}_2 + \text{hv} \rightarrow \text{Cl} + \text{ClOO} \\
\text{ClOO} + \text{M} \rightarrow \text{Cl} + \text{O}_2
\]

→ Cl\text{O}_2 must be stable and photolyze into Cl atoms
And of course, how to convert HCl and ClNO₃ into ClO?

Clouds with large optical depths observed over Antarctica and the Arctic by satellites – appear at ~195-196 K, too warm to be ice at 5 ppm of H₂O.
Even thicker clouds appear at 188 K, consistent with ice.

The two faces of NOₓ

Normally

\[ \text{HNO}_3 + h\nu \rightarrow \text{OH} + \text{NO}_2 \]
\[ \text{ClO} + \text{NO}_2 \rightarrow \text{ClNO}_3 \]

Over Antarctica

\[ \text{HNO}_3(g) + n\text{H}_2\text{O}(g) \rightarrow \text{HNO}_3(\text{H}_2\text{O})_n(s) \]
\[ \text{HCl}(g) + \text{HNO}_3(\text{H}_2\text{O})_n(s) \rightarrow \text{HCl}_a/\text{HNO}_3(\text{H}_2\text{O})_n(s) \]
\[ \text{HCl}(a) + \text{ClNO}_3(g) \rightarrow \text{Cl}_2 + \text{HNO}_3(s) \]

Sedimentation = irreversible removal of NOₓ

\[ \text{ClO} + \text{NO}_2 \rightarrow \text{ClNO}_3 \]
Lots of reactions that activate chlorine and produce HNO₃

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ice</th>
<th>NAT</th>
<th>SAT</th>
<th>Liquid</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO₃NO₂ + HCl → Cl₂ + HNO₃</td>
<td>0.2</td>
<td>0.1</td>
<td>~10⁻⁶</td>
<td>~10⁻⁷</td>
<td>~10⁻⁷</td>
</tr>
<tr>
<td>N₂O₅ + HCl → Cl₂O₂ + HNO₃</td>
<td>0.05</td>
<td>1 × 10⁻³</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>HCl + HCl → Cl₂ + H₂O</td>
<td>0.3</td>
<td>0.1</td>
<td>&gt;1 × 10⁻⁴</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>ClO₃NO₂ + H₂O → HOC₂ + HNO₃</td>
<td>0.1</td>
<td>1 × 10⁻⁴</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>N₂O₅ + H₂O → HOC₂ + HNO₃</td>
<td>3 × 10⁻⁴</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄ + HCl → HOC₂ + HNO₃</td>
<td>0.02</td>
<td>1 × 10⁻⁴</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

Why 195 K?

**TABLE 12.5** Some Values of Reaction Probabilities (γ) for the Heterogeneous Chlorine Activation Reactions under Typical Stratospheric Conditions

- Ice, NAT, SAT values are typical for polar regions
- Liquid values are typical for high latitudes
- H₂SO₄-HNO₃, H₂O values are typical for low latitudes

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1. From DeMore et al. (1992) and Rosenkranz et al. (1996) and references therein.
2. NAT = nitric acid trihydrate (solid), SAT = solid nitric acid trihydrate (solid).
3. Rosenkranz and K selects (1990); Zhang et al. (1999a, b), see Fig. 12.25c.
4. From DeMore et al. (1992) and Rosenkranz et al. (1996) and references therein.
5. From DeMore et al. (1992) and Rosenkranz et al. (1996) and references therein.
6. See also references for further details.

Typical 20 km values in polar regions

**FIGURE 12.23** Temperature dependence of reaction rates: a) H₂O and N₂O₅, typical for polar regions; b) ClO₃NO₂ and Cl₂O₂, typical for tropical regions.

**FIGURE 12.24** Reaction rates for H₂SO₄-HNO₃ and H₂O, typical for high and low latitudes, respectively.

**FIGURE 12.25** Typical measured reaction probabilities for (a) H₂SO₄-HNO₃, (b) H₂O, and (c) H₂O-HNO₃ for different surface conditions that can be present and provide heterogeneous laboratory results under typical tropospheric conditions.

Depends on the amount of surface water; see Rosenkranz et al. (1997) and references therein.
It’s both chlorine AND bromine (about 50/50)

\[
\begin{align*}
\text{ClO} + \text{BrO} & \rightarrow \text{products} \quad k_{\text{BrO}} \sim 10^{-11} \text{ cm}^{-3} \text{ s}^{-1} \\
\text{ClO} + \text{ClO} + \text{M} & \rightarrow \text{Cl}_2\text{O}_2 + \text{M} \quad k_{\text{ClO}} [\text{M}] \sim 10^{-13} \text{ cm}^{-3} \text{ s}^{-1}
\end{align*}
\]

\[
\begin{align*}
\text{ClO} & \sim 1 \text{ ppb} \\
\text{BrO} & \sim 10 \text{ ppt}
\end{align*}
\]

**Why the poles?**

[Figure 12.46: Model-calculated cumulative loss of ozone from August 1 to the day of maximum ozone depletion as a function of stratospheric bromine \([\text{BrO}] = 12.5 \text{ ppb}, [\text{NO}_x] = 2 \text{ ppb}, 70\% \text{ at an altitude corresponding to 50 mb total pressure in these calculations} (\text{adapted from Forster et al., 1986}).]

[Figure 10.13: Chronology of the Antarctic ozone hole.]
Scientists go back and reexamine other latitudes based on a new understanding of heterogeneous chemistry and aerosols in the lower stratosphere.

The story continues…