Heterogeneous and Homogeneous Stratospheric Chemistry
or "Everything You Ever Wanted To Know About Ozone (But Were Afraid To Ask)"

Rowland and Cicerone made UCI famous by their research on the mechanism of ozone hole formation.

http://ozonewatch.gsfc.nasa.gov/monthly/index.html
“Good Ozone”: Stratospheric Ozone Layer

Sample ozone height profiles measured by Stratospheric Aerosol and Gas Experiment II (SAGE II) (Image taken from “Stratospheric Ozone Textbook”)

SAGE O₃ Profile 940911 (40°S, 105°E)

Sample ozone height profiles measured by Stratospheric Aerosol and Gas Experiment II (SAGE II) (Image taken from “Stratospheric Ozone Textbook”)

SAGE O₃ Profile 940911 (40°S, 105°E)
"Bad Ozone": Tropospheric Smog

LA smog in the forties

Plant damage

LA smog today

Health effects
Why Do We Care About Stratospheric Ozone?

It is important to make a distinction between the troposphere ozone ("bad ozone") and stratospheric ozone ("good ozone"). Bad ozone is generally increased by anthropogenic air pollution. Good ozone is generally decreased by certain air pollutants.

- Sun emits a broad spectrum of colors extending far into the vacuum UV range
- Stratospheric ozone absorbs UV radiation < 300 nm, which is harmful to life. Atmospheric oxygen and nitrogen take care of vacuum UV radiation.
- Anthropogenic influence decrease stratospheric ozone both globally and locally (ozone hole). The largest effect comes form CFCs (chlorofluorocarbons).

FIGURE 13.15 Normalized action spectra taking response = 1.0 at 300 nm (adapted from Madronich, 1992).
Because of the importance of stratospheric ozone, its level has been tracked since about 1970 with various satellites. Nimbus-4 satellite carried the first **TOMS (Total Ozone Mapping Spectrometer)** onboard. TOMS spectrometers provide global ozone maps on a day to day basis. Because they work by measuring sun's radiation reflected from the atmosphere, *they only provide data for sunlit areas.*
Ozone Hole Evolution as Measured by TOMS
Stratospheric ozone depletion is not limited to the polar regions; the effect is also detectable on a global scale!
Until recently the Earth Probe TOMS (Total Ozone Mapping Spectrometer) was the only NASA spacecraft in orbit specializing in ozone retrieval. New Earth Observing System spacecraft (launched this summer) has a novel Ozone Monitoring Instrument (OMI) onboard. It will continue measurements of global total ozone trends started in 1970 with Nimbus-4.

http://aura.gsfc.nasa.gov/spacecraft/index.html
Long Awaited Aura Launch!

Earth Observing System (EOS) Aura is a NASA mission to study the Earth's ozone, air quality and climate. Aura Satellite Launched Successfully on July 15, 2004 from Vandenberg Air Force Base, CA.
Ground Based Measurements of Ozone

- Space measurements are complemented by an array of ground based observations.
- Dobson and Brewer spectrometers are standard devices for measurement of slant column densities. Dobson spectrometer uses wavelength pairs in near UV/Blue to determine optical depth and calculate ozone column density.
- Vertical column density units are molecules cm\(^{-2}\). For ozone, "Dobson units" is used: 100 DU = 1 mm of ozone at STP.
- Typical ozone column is 300 DU = 8 \times 10^{18} molecules cm\(^{-2}\). For comparison, total air column = 2.7 \times 10^{25} molecules cm\(^{-2}\).
With only a few measurements of the total ozone column and its latitudinal variation, Sir Sidney Chapman was the first to attempt to quantitatively explain ozone in Earth’s atmosphere.

**Chapman mechanism:**

1. $\text{O}_2 + hv \rightarrow \text{O} + \text{O}$  \hspace{1cm} J$_{\text{O}_2} \approx 10^{-11}$ s$^{-1}$ at 30 km
2. $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}^*$  \hspace{1cm} $k_2 \approx 9 \times 10^{-34}$ cm$^6$/molec$^2$ s$^{-1}$ at 250 K
3. $\text{O}_3 + hv \rightarrow \text{O}_2 + \text{O}$  \hspace{1cm} J$_{\text{O}_3} \approx 10^{-3}$ s$^{-1}$ at 30 km
4. $\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$  \hspace{1cm} $k_4 \approx 2 \times 10^{-15}$ cm$^3$/molec s$^{-1}$ at 250 K

Sidney Chapman Cycle (1930)

![Ozone Cycle Diagram](image)
We can now calculate the concentration of ozone at steady state from Chapman's mechanism. We assume that the rate of production of odd oxygen is balanced by the rate of loss of odd oxygen:

$$\frac{d[O_x]}{dt} = 2J_{O_2}[O_2] - 2k_4[O][O_3] \sim 0$$

$$J_{O_2}[O_2] = k_4[O][O_3] = k_4J_{O_3}[O_3]^2/(k_2[O_2][M])$$

The timescale for establishing this steady-state is quite fast: Even at 50 km, $$k_2[O_2][M]$$ is $$= 0.05 \text{ s}^{-1}$$. $$J_{O_3}$$ is much smaller than this and so, $$[O]/[O_3] \ll 1$$.

We can now calculate the concentration of ozone at steady state from Chapman’s mechanism. We assume that the rate of production of odd oxygen is balanced by the rate of loss of odd oxygen:

$$[O_3]^2 = J_{O_2}k_2[O_2]^2[M]/(k_4J_{O_3})$$

**“Odd Oxygen”**

The rate of interconversion between O and O₃ is MUCH faster than either the production of O from O₂ photolysis or the loss of ozone via reaction with O. It is therefore useful to define a “family” of odd oxygen species:

$$O_x = O + O_3$$

The partitioning between O and O₃ is set by reactions 2 and 3 (steady-state):

$$k_2[O][O_2][M] = J_{O_3}[O_3]$$

$$[O]/[O_3] = J_{O_3}/(k_2[O_2][M])$$

The timescale for establishing this steady-state is quite fast: Even at 50 km, $$k_2[O_2][M]$$ is $$= 0.05 \text{ s}^{-1}$$. $$J_{O_3}$$ is much smaller than this and so, $$[O]/[O_3] \ll 1$$.

Solve in class: Derive this relationship and calculate the expected $$[O_3]$$ at 30 km using the J values and rate constants given on the previous page. (A: 8.7 ppm)

Estimate the lifetimes for O and O₃ with respect to all the processes shown in the figure at 30 km ($T=250 \text{ K; } P = 10 \text{ Torr}$). (A: see next pages)

Estimate the $$[O]/[O_3]$$ ratio. (A: $$3.5\times10^{-5}$$)
Concentrations from the Chapman Cycle

\[
\frac{d[O_X]}{dt} = 2J_{O_2}[O_2] - 2k_Y[O][O_3] = 0
\]

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

\[
\frac{d[O]}{dt} = -k_2[O][O_2]CH + J_{O_3}[O_3] = 0 \quad \text{(fast processes only)}
\]

\[[O_3] = \frac{J_{O_3}[O_3]}{k_2[O_2]CH}\]

Combine:

\[J_{O_2}[O_2] = k_Y[O][O_3] \cdot \frac{J_{O_3}[O_3]}{k_2[O_2]CH}\]

\[\left\{ \frac{J_{O_2} \cdot k_2 \cdot [O_2]^{2} \cdot [CH]}{k_Y J_{O_3}} \right\}^{1/2}\]

\[\text{at } 280K @ 10 \text{ Torr} \quad \frac{[N]}{[N]} = \left(\frac{P}{kT}\right) = 3.87 \cdot 10^{17} \frac{\text{molec}}{\text{cm}^3}\]

\[J_{O_2} = 10^{-3} \text{ s}^{-1} \quad k_2 = 9 \cdot 10^{-34} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1} \quad J_{O_2} = 10^{-11} \text{ s}^{-1}\]

\[k_Y = 2.1 \cdot 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\]

\[\frac{[O_3]}{[O_2]} = \frac{J_{O_2}}{k_2[O_2]CH} = 3.5 \cdot 10^{-5}\]

\[\frac{[O_3]}{[N]} = 8.8 \text{ ppm}\]
Lifetimes of O and O$_3$

$\tau = \frac{1}{k_2 [O][N]} = \frac{1}{9 \cdot 10^{-34} \cdot 0.21 \cdot (3.9 \cdot 10^{17})^2} \approx 0.035 s$

$\tau = \frac{1}{k_4 [O_3]} = \frac{1}{2 \cdot 10^{-15} \cdot 3.4 \cdot 10^{12}} \approx 150 s$

$\tau = \frac{1}{j_{O_3}} = 10^3 s$

$\tau = \frac{1}{k_4 [O_3]} = \frac{1}{2 \cdot 10^{-15} \cdot 1.2 \cdot 10^8} = 4.2 \cdot 10^6 s$

$[O_3] = 3.4 \cdot 10^{12}$ molec/cm$^3$

$[O] = 3.5 \cdot 10^5$, $[O_3] = 1.2 \cdot 10^8$ molec/cm$^3$
Fig. 10-5 Chapman mechanism at low latitudes. Left panel: Lifetime of $O_x$. Center panel: $O_2$ and $O_3$ photolysis rate constants. Right panel: calculated and observed vertical profiles of $O_3$ concentrations.

From Jacob's "Atmospheric Chemistry"
Stratospheric Ozone: Effect of Radicals

\[ [O_3]_{\text{Chapman}} = 0.21 \times [M]^{3/2} \times \sqrt{\frac{J_{O_2} k_2}{J_{O_3} k_4}} \]

But what Sir Sidney Chapman didn’t know about was CATALYSIS:

**DECOMPOSITION**

- **HO\textsubscript{x} cycle**
  - OH \rightarrow HO\textsubscript{2} \rightarrow OH
  - Net: 2O\textsubscript{3} \rightarrow 3O\textsubscript{2}
  - 15 - 25 km

- **ClO\textsubscript{x} cycle**
  - Cl \rightarrow ClO \rightarrow Cl
  - Net: O + O\textsubscript{3} \rightarrow 2O\textsubscript{2}
  - Above 30 km

- **NO\textsubscript{x} cycle**
  - NO \rightarrow NO\textsubscript{2} \rightarrow NO
  - Net: O + O\textsubscript{3} \rightarrow 2O\textsubscript{2}
  - 35 - 45 km

**PRODUCTION**

\[ O + M + O\textsubscript{2} \rightarrow O_3 + M \]
Assume steady state partitioning:

\[ k_{\text{NO}+\text{O}_3}[\text{NO}][\text{O}_3] = k_{\text{NO}_2+\text{O}}[\text{NO}_2][\text{O}] + J_{\text{NO}_2}[\text{NO}_2] \]

\[-(d[\text{O}_\text{x}]/dt)_{\text{catalyzed}} = k_{\text{NO}+\text{O}_3}[\text{NO}][\text{O}_3] + k_{\text{NO}_2+\text{O}}[\text{NO}_2][\text{O}] - J_{\text{NO}_2}[\text{NO}_2] \]

\[ = 2 \times k_{\text{NO}_2+\text{O}}[\text{NO}_2][\text{O}] = 2 \times 6.5 \times 10^{-12} \times \exp(120/T)[\text{NO}_2][\text{O}] \]

Compare to Chapman sink (\(k_4\)):

\[-(d[\text{O}_\text{x}]/dt)_{\text{Chapman}} = 2 \times k_{\text{O}+\text{O}_3}[\text{O}][\text{O}_3] = 2 \times 8.0 \times 10^{-12} \times \exp(-2060/T)[\text{O}][\text{O}_3] \]

Find the relative importance by dividing the rates by each other:

\[ \text{Catalyzed/Chapman} = \frac{k_{\text{NO}_2+\text{O}}}{k_{\text{O}+\text{O}_3}} \times \frac{[\text{NO}_2]}{[\text{O}_3]} \]

This ratio ranges from about 1 in winter to over 10 in summer.

Conclusion: \(\text{NO}_x\) cycle is comparable to Chapman in efficiency!
Sources of Stratospheric NO\textsubscript{x}: N\textsubscript{2}O

N\textsubscript{2}O source:

- O\textsubscript{3} + hv → O\textsubscript{2} + O(\textsuperscript{1}D) \quad J\textsubscript{O3}
- N\textsubscript{2}O + hv → N\textsubscript{2} + O(\textsuperscript{1}D) \quad J\textsubscript{N2O}
- N\textsubscript{2}O + O(\textsuperscript{1}D) → N\textsubscript{2} + O\textsubscript{2} \quad k\textsubscript{2a}

→ NO + NO \quad k\textsubscript{2b}

What is the yield of NO from N\textsubscript{2}O?

k\textsubscript{2a} = 5 \times 10^{-11}; \quad k\textsubscript{2b} = 6.7 \times 10^{-11}

N\textsubscript{2}O lifetime: \quad (1.2 \times 10^{-10}[O(\textsuperscript{1}D)] + J\textsubscript{N2O})^{-1}

At 35 km, yield of NO\textsubscript{x} from N\textsubscript{2}O

= 2 \times 6.7 \times 10^{-11} \times 80 / 1.6 \times 10^{-7} = 0.07

**Conclusion:** Significant amount of NO\textsubscript{x} is produced from N\textsubscript{2}O.

<table>
<thead>
<tr>
<th>Z (km)</th>
<th>[O(\textsuperscript{1}D)] (mol/cm\textsuperscript{3})</th>
<th>J\textsubscript{N2O} (sec\textsuperscript{-1})</th>
<th>(\tau) (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5</td>
<td>3 \times 10^{-10}</td>
<td>75</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
<td>4 \times 10^{-8}</td>
<td>1.5</td>
</tr>
<tr>
<td>35</td>
<td>80</td>
<td>1.5 \times 10^{-7}</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>
Concern: There is a rapid change in N$_2$O abundance. The consequences of this N$2$O rise on the stratospheric ozone budget are still unclear. IPCC 2007
Gas-Phase chemistry:

\[ \text{OH} + \text{NO}_2 \rightarrow \text{HONO}_2 \]  \hspace{1cm} (1)

\[ \text{OH} + \text{HONO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_3 \]  \hspace{1cm} (2)

\[ \text{HONO}_2 + h\nu \rightarrow \text{OH} + \text{NO}_2 \]  \hspace{1cm} (3)

Steady-State:

\[ k_1[\text{OH}][\text{NO}_2] = \{k_2[\text{OH}] + J_3\} \times [\text{HONO}_2] \]

\[ [\text{HONO}_2] = \frac{k_1[\text{OH}][\text{NO}_2]}{\{k_2[\text{OH}] + J_3\}} \]

\[ \left\{ \frac{[\text{NO}_2]}{[\text{HONO}_2]} \right\}_{\text{Gas}} = \frac{k_2[\text{OH}] + J_3}{k_1[\text{OH}]} \]

Evaluating this expression for the \([\text{NO}_2]/[\text{HONO}_2]\) ratio we find:

\[ \approx 1 \text{ at } 30 \text{ km} \]

\[ \approx 0.2 \text{ at } 20 \text{ km} \]

Below 25 km, particularly in winter it is observed that the measured ratio of \(\text{NO}_2\) to \(\text{HONO}_3\) is much smaller than calculated via this chemistry. We now know that this is due to the heterogeneous reaction:

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HONO}_2 \]
Catalysis by "Odd Hydrogen"

The "odd hydrogen" radicals, HO$_x$ = OH and HO$_2$, are central to the photochemistry of the stratosphere and troposphere. These radicals participate in many catalytic loss mechanisms for ozone:

I. \[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad (1)
\]
\[
\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \quad (2) - \text{rate determining step}
\]
\[
\text{Net: O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 \quad \text{(Same as Chapman)}
\]

\[
k_2/k_{\text{Chapman}} = 1 \times 10^5 @ 240 \text{ K}!
\]

\[
([\text{HO}_2]/[\text{O}_3])_{40\text{km}} = 1 \times 10^7 \text{ mol cm}^{-3} / 1 \times 10^{12} \text{ mol cm}^{-3} = 1 \times 10^{-5}
\]

Result: \textit{Comparable importance!}
More HO\textsubscript{x} Cycles:

II.

\begin{align*}
\text{OH} + \text{O} &\rightarrow \text{O}_2 + \text{H} \quad (1) \\
\text{H} + \text{O}_2 + \text{M} &\rightarrow \text{HO}_2 + \text{M} \quad (2) \\
\text{HO}_2 + \text{O} &\rightarrow \text{OH} + \text{O}_2 \quad (3)
\end{align*}

\textbf{Net:} \text{O} + \text{O} \rightarrow \text{O}_2

III.

\begin{align*}
\text{OH} + \text{O}_3 &\rightarrow \text{HO}_2 + \text{O}_2 \quad (1) \\
\text{HO}_2 + \text{O}_3 &\rightarrow \text{OH} + \text{O}_2 \quad (2)
\end{align*}

\textbf{Net:} \text{O}_3 + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + \text{O}_2

\textit{NB: No atomic O!}

\text{HO}_x \text{ Cycling time very fast:}

\tau_{\text{OH} \rightarrow \text{HO}_2} = \frac{1}{k_{\text{OH} + \text{O}_3} [\text{O}_3]} = 10 \text{ s}

(240 K, [\text{O}_3] = 3 \times 10^{12} \text{ molecules cm}^{-3})
**HO\textsubscript{x} Sources (Stratosphere)**

*Primary*: breaking O-H bond in H\textsubscript{2}O or C-H bond in CH\textsubscript{4}:

O (\textsuperscript{1}D) + H\textsubscript{2}O → 2 OH (90%)

O (\textsuperscript{1}D) + CH\textsubscript{4} → OH + CH\textsubscript{3}

*Note 1*: CH\textsubscript{4} level more than doubled in the industrial era!

*Note 2*: Stratospheric H\textsubscript{2}O partly comes from CH\textsubscript{4}

*Secondary*: release of HO\textsubscript{x} from “reservoir” compounds such as :

HONO\textsubscript{2} + \textit{hv} → OH + NO\textsubscript{2}

HOBr + \textit{hv} → OH + Br

**HO\textsubscript{x} Sinks (Stratosphere)**

I. OH + HO\textsubscript{2} → H\textsubscript{2}O + O\textsubscript{2} \quad \text{\(k = 5 \times 10^{-11} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\)}

II. OH + NO\textsubscript{2} + M → HONO\textsubscript{2} + M \quad III. HO\textsubscript{2} + NO\textsubscript{2} + M → HO\textsubscript{2}NO\textsubscript{2} + M

OH + HONO\textsubscript{2} → H\textsubscript{2}O + NO\textsubscript{3}

NO\textsubscript{3} + \textit{hv} → NO\textsubscript{2} + O (mostly)

Net: OH + OH → H\textsubscript{2}O + O

Net: OH + HO\textsubscript{2} → H\textsubscript{2}O + O\textsubscript{2}

**Conclusion**: HO\textsubscript{x} and NO\textsubscript{x} cycles are strongly coupled
Stratospheric OH and HO$_2$ measurements

**Fig. 4.** Altitude profile of OH. The mixing ratio of OH is plotted versus altitude for four profiles. High-altitude measurements were made from a balloonborne experiment, while the lower altitudes were sampled by the NASA ER-2 aircraft. Shown at the beginning and end of each profile is the solar zenith angle (SZA). The dependence of OH on SZA increases lower in the atmosphere due to the increasing attenuation of the ultraviolet solar radiation that is required to produce the odd-hydrogen radicals.

**Fig. 5.** Diurnal variation of OH and HO$_2$ observed near 18-km altitude on 11–12 May 1993 during the SPADE experiment (taken from Salawitch et al. 1994). Results from a photochemical model are also displayed. A model that neglects heterogeneous chemistry occurring on sulfuric acid aerosols (dashed line) underestimates OH and HO$_2$ by large amounts. Low SZA measurements are described within the experimental uncertainty by a model that includes the heterogeneous hydrolysis of N$_2$O$_5$ (dark line). This model, however, also underestimates the HO$_2$ concentrations at high SZAs. A model that includes a speculated heterogeneous reaction producing HONO (gray line) accurately describes the observations throughout the day.
Stratospheric Halogens

As with NO\textsubscript{x}, and HO\textsubscript{x}, chlorine radicals catalyze the loss of ozone. Stolarski and Cicerone pointed out that the reaction:

\[
O + ClO \rightarrow Cl + O\textsubscript{2}
\]

is very fast \((\sim 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})\) and therefore the cycle:

\[
\begin{align*}
Cl + O\textsubscript{3} & \rightarrow ClO + O\textsubscript{2} \\
ClO + O & \rightarrow Cl + O\textsubscript{2} \quad \text{(RDS)}
\end{align*}
\]

**Net:** \(O + O\textsubscript{3} \rightarrow O\textsubscript{2} + O\textsubscript{2}\)

would be very efficient if a stratospheric source of chlorine existed. They suggested solid rocket fuel could be important.

In the lower stratosphere a second cycle is also important:

\[
\begin{align*}
ClO + HO\textsubscript{2} & \rightarrow HOCl + O\textsubscript{2} \quad \text{(RDS)} \\
HOCl + hv & \rightarrow OH + Cl \\
OH + O\textsubscript{3} & \rightarrow HO\textsubscript{2} + O\textsubscript{2} \\
Cl + O\textsubscript{3} & \rightarrow ClO + O\textsubscript{2}
\end{align*}
\]

**Net:** \(O\textsubscript{3} + O\textsubscript{3} + hv \rightarrow O\textsubscript{2} + O\textsubscript{2} + O\textsubscript{2}\)
CFCs Destroy Ozone Catalytically!

**Chapman cycle:**
\[
\begin{align*}
O_2 + hv & \rightarrow 2O \\
O + O_2 & \rightarrow O_3 \\
O_3 + hv & \rightarrow O + O_2
\end{align*}
\]

**Perturbation by CFCs:**
\[
\begin{align*}
CF_2Cl_2 + hv & \rightarrow Cl + CF_2Cl \\
Cl + O_3 & \rightarrow ClO + O_2 \\
ClO + O_3 & \rightarrow Cl + O_2
\end{align*}
\]

**FIGURE 1.8** Measured concentrations of the chlorine monoxide free radical (ClO) as well as O₃ outside and inside the polar vortex on August 23, 1987 (adapted from Anderson, 1989).
Experimental Evidence of Cl/ClO Ozone Loss

Free Radicals Within the Antarctic Vortex: The Role of CFCs in Antarctic Ozone Loss
The natural background for stratospheric chlorine (from CH$_3$Cl production in surface ocean) would be ~ 500 pptv.

Anthropogenic CFCs (chlorofluorocarbons) have comparable concentrations.

*In their famous 1973 paper, Roland and Molina (UCI) pointed out that the photolysis of freons CF$_2$Cl$_2$ (CFC-12) and CFCl$_3$ (CFC-11) in the upper stratosphere is the major source of stratospheric chlorine.*

HCFCs are replacing the CFCs in refrigeration because the majority of the HCFCs are degraded in the troposphere via OH reactions.

The HCFCs are scheduled to be eliminated in the next several decades to be replaced by compounds that contain no chlorine or bromine.
Inorganic Chlorine “Reservoirs”

Once the "organic halogens" (called CCl\textsubscript{y}) are degraded to "inorganic chlorine" compounds (Cl\textsubscript{y}), two important inorganic chlorine “reservoir” (non-radical) compounds, HCl and ClONO\textsubscript{2} are formed.

**HCl:**

**Produced via:**

\[
\begin{align*}
\text{Cl} + \text{CH}_4 & \rightarrow \text{HCl} + \text{CH}_3 \\
\text{and} & \\
\text{OH} + \text{ClO} & \rightarrow \text{HCl} + \text{O}_2 \quad (6\% \text{ yield}).
\end{align*}
\]

**Lost via:**

\[
\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl} \quad \text{(also a sink of HO}_x\text{)}
\]

**Calculated lifetime of HCl:**

\[
\tau_{\text{HCl}} = \frac{1}{k_{\text{OH}+\text{HCl}}}[\text{OH}] \\
\approx 100 \text{ days @ } 20 \text{ km; 10 days @ } 40 \text{ km}
\]

**ClONO\textsubscript{2}:**

**Produced via:**

\[
\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2
\]

**Lost via:**

\[
\text{ClONO}_2 + \text{hv} \rightarrow \text{ClO} + \text{NO}_2
\]

\[
J_{\text{ClONO}_2} \quad (10 \rightarrow 30 \text{ km}) \sim 5 \times 10^{-5} \text{ s}^{-1}
\]

\[
\tau_{\text{ClONO}_2} = \frac{1}{J_{\text{ClONO}_2}} = 5 \text{ hours}
\]
In the absence of industrial halocarbon production, the natural background for stratospheric chlorine ($\text{CH}_3\text{Cl}$ production in surface ocean) would be $\sim 500$ pptv.

In their famous 1973 paper, Roland and Molina (UCI) pointed out that the photolysis of freons ($\text{CF}_2\text{Cl}_2$ – CFC-12 - and $\text{CFCl}_3$ - CFC-11) in the upper stratosphere is the major source of stratospheric chlorine. This process (photolysis in the stratosphere) is the only known loss mechanism for most of the fully halogenated alkanes.
Chlorine Inventory

- Total chlorine mixing ratio, $C_{\text{total}}$, is constant => no significant sinks
- $\text{CCl}_y$ (CFCs + HCFCs) are converted into HCl and ClONO$_2$ at higher altitudes
- ClO, which is active in ozone destruction, is only a small fraction of $C_{\text{total}}$

Figure 2. A linear-scale presentation of the key components entering in the total Cl-loading evaluation throughout the stratosphere at northern midlatitudes. The $\text{CCl}_y$ curve refers to the total chlorine bound in all organic source gases listed in the text. $\text{Cl}_{\text{TOT}}$ represents the summation over $\text{CCl}_y$, HCl, ClONO$_2$, ClO, HOCI and COClF.
Methyl Bromide and Halons

- CH$_3$Br has both natural and anthropogenic sources. The relative strengths of these sources is uncertain.
- CH$_3$Br contributes ~½ of total stratospheric bromine.
- CH$_3$Br and halons (Br-containing haloalkanes) were banned under the Montreal protocol and its amendments. The main motivation for this ban is **much larger ozone destruction efficiency of Br/BrO compared to Cl/ClO**.

Effective relative contributions of different gases to ozone destruction as estimated by CSIRO Marine and Atmospheric Research (Australia).

CH$_3$Br and halon contributions are large despite their smaller concentration relative to CFCs.
Why is Br More Efficient Than Cl?

I. The rate coefficients are faster

\[ \text{HO}_2 + \text{BrO} \rightarrow \text{HOBr} + \text{O}_2 \] is 10 times faster than \[ \text{HO}_2 + \text{ClO} \]

II. New ozone loss mechanisms

\[ \text{ClO} + \text{BrO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2 \quad k \sim 1 \times 10^{-11} \]
\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]
\[ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \]
Net: \[ \text{O}_3 + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 \]

III. Organic bromine compounds degrade faster

\( \text{Br}_y \) is liberated from \( \text{CBr}_y \) faster than chlorine.

IV. A much larger fraction of \( \text{Br}_y \) is in radical form

The reaction \( \text{Br} + \text{CH}_4 \) is significantly endothermic. Thus \( \text{HBr} \) is not an important reservoir. [\( \text{BrO} \)] is generally 5-10 pptv, only 5 times smaller than [\( \text{ClO} \)] in lower stratosphere.
The Show So Far

Ozone is produced by photolysis of $O_2$ shortward of 200 nm

Ozone is lost via $O_x$, $NO_x$, $HO_x$, and Halogen radical chemistry

The following are the rate determining steps:

\[
O + O_3 \rightarrow O_2 + O_2 \\
O + NO_2 \rightarrow NO + O_2 \\
O + HO_2 \rightarrow OH + O_2 \\
O + ClO \rightarrow Cl + O_2 \\
HO_2 + O_3 \rightarrow OH + O_2 + O_2 \\
HO_2 + ClO/BrO (+ hv) \rightarrow OH + Cl/Br + O_2
\]

In the middle and upper stratosphere (above 30 km) the photochemical lifetime of ozone is short (week/day) and ozone is determined by chemistry alone.

In the lower stratosphere, the ozone lifetime becomes long and transport is critical for determining the local concentration of ozone. Chemistry is also important but to understand its role we must consider chemistry integrated along the path taken by the ozone during its lifetime.
Summary of Gas-Phase Chemistry

Nitrogen oxides
- NO\textsubscript{x} is key free radical catalyst for ozone removal
- NO\textsubscript{x} is formed by oxidation of N\textsubscript{2}O
- [NO\textsubscript{x}]/[NO\textsubscript{y}] ratio is critical for understanding ozone loss
- NO\textsubscript{x} could be perturbed by stratospheric aircraft

Halogens
- Halogens are very potent catalysts for ozone loss
- Halogen concentrations grew dramatically between 1970 and 1990 due to release of industrial halocarbons
- In upper stratosphere evidence of chlorine-related loss of ozone is very strong
- In lower stratosphere both chlorine and bromine contribute to mid-latitude ozone loss
- In lower stratosphere, efficiency of ozone loss by chlorine decreases as NO\textsubscript{2} increases due to sequestration of Cl\textsubscript{y} into ClONO\textsubscript{2}

HO\textsubscript{x} family
- There is 1-10 pptv of OH in the stratosphere during daylight
- OH and HO\textsubscript{2} catalyze ozone loss in the stratosphere (particularly important above 35 and below 20 km)
- Primary HO\textsubscript{x} produced via O(\textsuperscript{1}D) + H\textsubscript{2}O; H\textsubscript{2}O increasing due to increasing CH\textsubscript{4}
- Sink via OH + HO\textsubscript{2} and interaction with NO\textsubscript{2} – lifetime ~ few min
Heterogeneous Chemistry and Polar Ozone
1988 Mozurkewich and Calvert measured a high reactive uptake of \( \text{N}_2\text{O}_5 \) on aqueous solutions:

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O}(s) \rightarrow 2 \text{HONO}_2 \]

Recall that \( \text{N}_2\text{O}_5 \) is produced at night from \( \text{NO}_x \):

\[
\begin{align*}
\text{NO} & \underset{O_3}{hv(10^{-2} \text{ s}^{-1})} \text{NO}_2 \\
\text{NO}_2 & \underset{O_3}{hv(10^{-1} \text{ s}^{-1})} \text{NO}_3 \\
\text{NO}_3 & \underset{\text{NO}_2}{hv(10^{-5} \text{ s}^{-1})} \text{N}_2\text{O}_5 \rightarrow 2\text{HONO}_2
\end{align*}
\]

This chemistry converts \( \text{NO}_x \) to \( \text{HNO}_3 \) greatly reducing the concentration of \( \text{NO}_2 \) particularly during winter when the photolysis rate of \( \text{N}_2\text{O}_5 \) is reduced.

During winter, the ratio \([\text{NO}_2]/[\text{HONO}_2]\) is about 1/2 to 1/3 of the expected value if only gas phase chemistry converted \( \text{NO}_2 \) to \( \text{HONO}_2 \).

This profoundly alters the concentration of \( \text{HO}_2 \) and \( \text{ClO} \) in the lower stratosphere because \( \text{NO}_x, \text{HO}_x, \) and \( \text{ClO}_x \) are all coupled to each other.
The estimated impact of $\text{N}_2\text{O}_5$ hydrolysis: the lower stratosphere is much more sensitive to chlorine / bromine than thought earlier. One modest volcano can increase the ratio of $\text{ClO}/\text{Cl}_y$ from 0.02 to 0.03 – i.e. 50% increase in halogen catalyzed ozone loss; an effect equivalent to the entire increase in $\text{Cl}_y$ during the 1990s.
During winter, radiative cooling produces low pressure region over the poles. This results in a strong "polar nighttime jet" that is quite circular in the S.H. but more distorted in the north. Temperatures begin to fall as sunlight leaves the poles and cooling continues through the winter. When temperatures are low enough PSCs (polar stratospheric clouds) start to form.

Figure 1.7.1-1  The range, near 90 mb, of minimum brightness temperatures poleward of 20° latitude (deduced from channel 24 of the MSU), computed daily for winter and spring from 1980 to 1988. The location of the minimum temperature is near the pole in winter, but moves to low latitudes during spring. Solid lines and heavy shading correspond to the Southern Hemisphere from June to October (upper labels in the time axis). Dashed lines correspond to the Northern Hemisphere from December to April (lower labels on the time axis). The horizontal lines across the figure represent the temperatures below which type I and type II PSCs can form (from Mechoso et al., 1989).
PSCs

POSSIBLE PHASES AND COMPOSITIONS OF PARTICULATES IN THE STRATOSPHERE

Background Aerosols
- Liquid H$_2$SO$_4$/H$_2$O solutions (T > 200 K)
- Crystalline sulfuric acid tetrahydrate SAT (T < 210 K)

Type I PSCs (T < 196 K)
- Nitric acid trihydrate (NAT, HNO$_3$•3H$_2$O)
- Liquid H$_2$SO$_4$/HNO$_3$/H$_2$O solutions
- Nitric acid dihydrate (NAD, HNO$_3$•2H$_2$O)
- Crystalline ternary hydrate (H$_2$SO$_4$•HNO$_3$•5H$_2$O)
- Amorphous HNO$_3$/H$_2$O solutions (arbitrary compositions)

Type II PSCs (T < 188 K)
- Water ice

All the Cl$_y$ end up as ClO$_x$ in the polar vortex in winter. Are PSCs involved?

FIGURE 12.21 Schematic of polar stratospheric cloud (PSC) formation.
Table 3-1. Rates of heterogeneous reactions on polar stratospheric cloud particles and sulfate aerosol particles.

<table>
<thead>
<tr>
<th></th>
<th>PSCs</th>
<th>Sulfate Aerosols</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ice</td>
<td>HNO3 hydrates*</td>
</tr>
<tr>
<td>ClONO₂ + HCl → Cl₂ + HNO₃</td>
<td>Fast f(RH)b</td>
<td>Fast f(RH)b</td>
</tr>
<tr>
<td>HOCI + HCl → Cl₂ + H₂O</td>
<td>Fast f(RH)b</td>
<td>Fast f(RH)b</td>
</tr>
<tr>
<td>ClONO₂ + H₂O → HOCI + HNO₃</td>
<td>Fast Slow ¥</td>
<td>f(wt% H₂SO₄)b</td>
</tr>
<tr>
<td>N₂O₅ + H₂O → 2HNO₃</td>
<td>Fast Slow ¥</td>
<td>Fast</td>
</tr>
<tr>
<td>N₂O₅ + HCl → ClONO₂ + HNO₃</td>
<td>c c</td>
<td>c c</td>
</tr>
</tbody>
</table>

* Nitric acid trihydrate (NAT), nitric acid dihydrate (NAD)

** Rate is function of aerosol wt% H₂SO₄ or relative humidity (RH).

*** Unlikely to be fast, but not well studied

References: Abbatt and Molina, 1992a, b; Chu et al., 1994; Fried et al., 1994; Hanson and Ravishankara, 1991, 1992, 1994; Kolb et al., 1994; Middlebrook et al., 1992, 1994; Molina et al., 1993; Van Doren et al., 1991; Zhang et al., 1994

- **HCl** (lifetime weeks to months) and **ClONO₂** (lifetime ~ day) are converted to **Cl₂** (lifetime with respect to photolysis ~ ½ hour).
- **NOₓ** is converted into **HNO₃** (lifetime of many days).
- **HNO₃** sequestered on particles; can sediment leading to irreversible loss of **NOᵧ**.
Ozone Loss with PSCs Present

During the polar night, PSCs convert

a). $Cl_y$ into $ClO_x$

b). $NO_x$ into $HNO_3$

The ozone loss occurs very quickly when the sun comes out:

I. $ClO + BrO \rightarrow Br + Cl + O_2$

$Cl + O_3 \rightarrow ClO + O_2$

$Br + O_3 \rightarrow BrO + O_2$

II. $ClO + ClO + M \leftrightarrow ClOOCl + M$

$ClOOCl + hv (~350 \text{ nm}) \rightarrow Cl + Cl + O_2$

$2 (Cl + O_3 \rightarrow ClO + O_2)$

Each of these mechanism is responsible for approximately $\sim \frac{1}{2}$ of the polar ozone loss. Note that atomic oxygen is not required for either of these two schemes.
In northern hemisphere, ozone loss is not so severe and significant amounts of HNO\textsubscript{3} remain at end of winter. ClO\textsubscript{x} recovers into ClONO\textsubscript{2}.

In southern hemisphere, ozone loss goes to nearly completion (see earlier figure). As ozone goes down, the ratio Cl/ClO increases dramatically. With very little NO\textsubscript{x} remaining, ClO\textsubscript{x} is converted into HCl via Cl + CH\textsubscript{4}.

Fig. 10-13 Chronology of the antarctic ozone hole.
CFC Control Strategies

CFC control agreements:

- **Montreal protocol** (1987): Reduce/freeze production of CFCs and halons* (not enough!)
- **London amendments** (1990): Completely eliminate CFCs, halons, CCl₄ by 2000; CH₃CCl₃ by 2005
- **Copenhagen amendments** (1992): Eliminate CFCs, halons, CCl₄, CH₃CCl₃ by 1996; freeze CH₃Br
- **Vienna amendments** (1995): Freeze HCFCs, and eliminate them in 2020; eliminate CH₃Br in 2010

* Halons are similar to CFCs but they contain bromine; HCFCs contain some remaining H atoms.

**FIGURE 13.20** Estimated excess cases of skin cancer in the United States and northwestern Europe if no controls had been imposed on CFCs and halons and those under the Copenhagen Amendment (adapted from Slaper et al., 1996).