Stratospheric Chemistry
Part 1
(Chapter 4, p 155-169, 174-176, 198-222, 231-238)

• Ozone – Discovery and History
• The Stratosphere and circulation
• Chapman Chemistry
• Catalysts
• The Controversy
• The “Ozone Hole”
• International Regulations
The Human Connection

The EPA estimates that 60 million Americans born by the year 2075 will get skin cancer because of ozone depletion. About one million of these people will die. (thinkquest.org)

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).

DNA isn’t just for humans – plants and animals too!

FIGURE 13.15 Normalized action spectra taking response = 1.0 at 300 nm (adapted from Madronich, 1992).
Ozone History

In 1785, Martinus Van Marum noted “the odor of electrical matter” in the description of the discharge of air.

Note – this was before it was accepted that oxygen was even a component of air!
Officially named as a chemical in 1840 by Christian Schönbein, after he noted that it had a smell that was similar to that of phosphorus when exposed to air (Greek “ozein” for “to smell”)

It was soon realized that ozone was a good disinfectant. Marius Paul Otto was first to market a water purifier based on ozone – in the 1800s!
In 1923, Gordon Dobson developed the first spectrometer to measure ozone in the atmosphere, and he characterized its latitudinal seasonal variability. He shares credit for discovering that circulation of the stratosphere starts in the tropics and moves poleward.
Brewer-Dobson circulation 2

CH$_4$ (ppmv), circulation JANUARY

CH$_4$ (ppmv), circulation JULY

FIGURE 4.4 Zonally averaged ozone concentrations (in units of 10$^{-16}$ molecules cm$^{-2}$) as a function of altitude. March 32 (Herman, 1975). Ozone concentration at the equator peaks at an altitude of about 25 km. Over the poles the location of the maximum is between 15 and 20 km. At altitudes above the ozone bulge, O$_3$ formation is oxygen-limited; below the bulge, O$_3$ formation is photolimited.
1928 – Thomas Midgley develops chlorofluorocarbons for DuPont, inhaling them to prove that they nontoxic. These non-flammable compounds soon replace the deadly compounds (such as ammonia and SO\textsubscript{2}) in home refrigerators.

CFCs become popular in the 1960s when Americans want to live in sun belts, drive cars with air conditioning, and use spray cans for just about everything!

**FIGURE 12.11** Estimated annual worldwide releases of CFC-11 and CFC-12 from 1952 to 1980. Data from Chemical Manufacturers' Association (adapted from National Research Council, 1984).
In 1930, Sydney Chapman published several theoretical papers on upper-atmospheric ozone – now known as the “Chapman Cycle”

\[ \text{O}_2 + h\nu \rightarrow \text{O} + \text{O} \quad (\lambda < 242 \text{ nm}) \quad (1) \]

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

\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O} \quad (\lambda < 336 \text{ nm}) \quad (3) \]

\[ \text{O}_3 + \text{O} \rightarrow 2\text{O}_2 \quad (4) \]
rate 1 = \( J_{O_2}[O_2] \)  
\( (J_{O_2} \approx 10^{-11} \text{ s}^{-1}, 30 \text{ km}) \)

rate 2 = \( k_2[O][O_2][M] \)  
\( (k_2 \approx 9 \times 10^{-34} \text{ cm}^6\text{s}^{-1} \text{ at } 250 \text{ K}) \)

rate 3 = \( J_{O_3}[O_3] \)  
\( (J_{O_3} \approx 10^{-3} \text{ s}^{-1} \text{ at } 30 \text{ km}) \)

rate 4 = \( k_4[O][O_3] \)  
\( (k_4 \approx 2 \times 10^{-15} \text{ cm}^3\text{s}^{-1} \text{ at } 250 \text{ K}) \)

\[
\frac{d[O]}{dt} = 2J_{O_2}[O_2] - k_2[O][O_2][M] + J_{O_3}[O_3] - k_4[O][O_3]
\]

\[
\frac{d[O_3]}{dt} = k_2[O][O_2][M] - J_{O_3}[O_3] - k_4[O][O_3]
\]
We can see that this can easily become difficult to solve a series of reactions written in this way. It isn’t so much that the problem won’t become solvable, it that is there will be pieces of equations that have large values (“fast” rates) and others that are small, and solving these kinds of equations will necessarily require computers, and typically, computers don’t easily handle equations that have both large and small terms in them (these are called “stiff equations” because they require very small timesteps in order to get accurate answers.

Wikipedia: In mathematics, a **stiff equation** is a differential equation for which certain numerical methods for solving the equation are numerically unstable, unless the step size is taken to be extremely small. It has proven difficult to formulate a precise definition of stiffness, but the main idea is that the equation includes some terms that can lead to rapid variation in the solution.
FIGURE 12.15 Absorption cross sections for $\text{O}_2$ and $\text{O}_3$ from 120 to 360 nm, showing the window from $\sim 185$ to 210 nm (adapted from Rowland and Molina, 1975).
There is a simple numerical methods trick that we can use that will help separate out the large (fast) terms from the small (slow) ones. Note that if we define a new term, “odd oxygen” (or “$O_x$”), as the sum of $[O]$ and $[O_3]$, the cross terms in the equation (Chapman reactions 2 and 3) will cancel out. This is because neither reaction creates or destroys “odd oxygen’, they just cycle between the two forms – i.e., reactions (2) and (3) partition odd oxygen between $O$ and $O_3$.

$$\frac{d([O] + [O_3])}{dt} = \frac{d[O_x]}{dt} = 2J_{o_2}[O_2] - 2k_4[O][O_3]$$

We will call the term that forms $O_x$ the production term (P) and the term that destroys it the loss term (L), and the difference between these will be called “P minus L”, or $P - L$. 
“Odd oxygen”

Rate 1 = $J_{O_2} [O_2]$

Rate 2 = $k_2[O][O_2][M]$

Rate 3 = $J_{O_3} [O_3]$

Rate 4 = $k_4[O][O_3]$

\[
\frac{d([O] + [O_3])}{dt} = \frac{d[O_x]}{dt} = 2J_{O_2} [O_2] - 2k_4[O][O_3]
\]

In Steady State: \[
\frac{d[O_x]}{dt} = 0 = 2J_{O_2} [O_2] - 2k_4[O][O_3]
\]

(note, you get the same by assuming $O_2$ is in steady state)
You get a similar result assuming that $O_2$ is in steady state – the math is harder. Skip this slide if you don’t care about the math!

\[
\frac{d[O_2]}{dt} = -J_1[O_2] - k_2[O][O_2][M] + J_3[O_3] + 2k_4[O][O_3]
\]

\[
= -2J_1[O_2] + (J_1[O_2] - k_2[O][O_2][M] + J_3[O_3]) + 2k_4[O][O_3]
\]

\[
= -2J_1[O_2] + \frac{d([O] - [O_3])}{dt} + 2k_4[O][O_3]
\]

So, at steady state, both $d[O_2]/dt$ and the $d([O]-[O_3])dt$ terms will be zero. So that the following is true:

\[
J_1[O_2] = k_4[O][O_3]
\]
Note that this is an equation that defines a layer that has a peak somewhere above the surface. This is due to the fact that $J_{O_2}$ will be increasing with altitude (with less atmosphere above, there will be less absorption (Beer’s Law!), and $[M]^{3/2}$ will decrease with altitude.
Back to our problem – we can now solve for $O_3$

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

Substituting back:

$$\frac{d[O]}{dt} = k_2[O][O_2][M] + J_{O_3}[O_3] + k_4[O][O_3] \sim k_2[O][O_2][M] + J_{O_3}[O_3]$$

At steady state:

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

$$\frac{[O]}{[O_3]} = \frac{J_{O_3}}{k_2} \frac{1}{[O_2][M]}$$

$$[O_3] = 0.21 \left( \frac{k_2}{k_4} \right)^{\frac{1}{2}} \left( \frac{J_{O_2}}{J_{O_3}} \right)^{\frac{1}{2}} \left[ M \right]^{\frac{3}{2}}$$
Chapman chemistry (in steady state)

\[ O_2 + h\nu \rightarrow O + O \]
\[ O + O_2 + M \rightarrow O_3 + M \]
\[ O_3 + h\nu \rightarrow O_2 + O \]
\[ O_3 + O \rightarrow O_2 + O_2 \]

Slow and exactly balance

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

Fast and approx. balance

\[ k_2[O][O_2][M] \sim J_{O_3}[O_3] \]

\[ \frac{[O]}{[O_3]} \sim \frac{J_{O_3}}{k_2} \frac{1}{[O_2][M]} \]

\[ [O_3] \sim 0.21 \left( \frac{k_2}{k_4} \right)^{\frac{1}{2}} \left( \frac{J_{O_2}}{J_{O_3}} \right)^{\frac{1}{2}} [M]^{\frac{3}{2}} \]
How does this compare to observations? Chapman mechanism predicts more ozone than what is observed!

What’s missing?

$\text{Faster}$

$\text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2$

**FIGURE 12.5** Model-calculated ozone vertical profiles for a Chapman or O$_2$ model, with only O$_2$, O, and O$_3$ as reactive species and the reference atmosphere chosen to be typical of 1960 conditions (adapted from Kinnison et al., 1988).
We saw above that steady state ozone was determined by the ratio of production to loss, and that production (in the stratosphere, at least) is determined by a process that is dependent only on the abundance of \( O_2 \), which is relatively constant over time, and solar energy, which doesn’t vary that significantly. So the only explanation for the overprediction of ozone by Chapman theory is that there must be additional losses. These will be due to catalysts.
Water in the stratosphere would lead to catalytic destruction of ozone by ‘speeding up’ reaction (4) of Chapman’s mechanism – thus, introducing the concept of catalytic destruction of ozone

\[
\begin{align*}
H + O_3 & \rightarrow OH + O_2 \\
OH + O & \rightarrow H + O_2 \\
\text{Net} - O_3 + O & \rightarrow O_2 + O_2
\end{align*}
\]

Catalysis

\[
\begin{align*}
\text{H} + \text{O}_3 & \rightarrow \text{OH} + \text{O}_2 \quad \text{rate} = k_a[\text{H}][\text{O}_3] \\
\text{OH} + \text{O} & \rightarrow \text{H} + \text{O}_2 \quad \text{rate} = k_b[\text{OH}][\text{O}] \\
\text{Net} - \text{O}_3 + \text{O} & \rightarrow \text{O}_2 + \text{O}_2
\end{align*}
\]

\[
\frac{d[\text{O}_3]}{dt} \approx -2k_4[\text{O}][\text{O}_3] - 2k_b[\text{OH}][\text{O}]
\]

Replace \(k_4[\text{O}][\text{O}_3]\) with apparent loss

\[
k_4^{\text{app}} = k_4 \left[ 1 + \frac{k_b[\text{OH}]}{k_4[\text{O}_3]} \right]
\]

\[
[\text{O}_3] = 0.21^2 \left( \frac{k_2}{k_4^{\text{app}}} \right)^{\frac{1}{2}} \left( \frac{J_{\text{O}_2}}{J_{\text{O}_3}} \right)^{\frac{1}{2}} [M]^{\frac{3}{2}}
\]

\(> k_4\)
Paul J. Crutzen

"Influence of Nitrogen Oxides on Atmospheric Ozone Content"

$$\text{N}_2\text{O} + \text{O}^1(\text{D}) \rightarrow \text{NO} + \text{NO}$$
Formation of NO\textsubscript{x}

\[
\begin{align*}
O_3 + h\nu & \rightarrow O_2 + O(^1D) & J_{O_3} \\
N_2O + h\nu & \rightarrow N_2 + O(^1D) & J_{N2O} \\
N_2O + O(^1D) & \rightarrow N_2 + O_2 \\
& \rightarrow NO + NO & k_{2a} = 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \\
& & k_{2b} = 6.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}
\end{align*}
\]

About 3-4\% of the loss of N\textsubscript{2}O in the stratosphere results in the formation of nitric oxide (NO), which then acts as the main catalyst for ozone destruction. Since much of the N\textsubscript{2}O is from natural processes, this is considered a natural loss for ozone. And it is just the additional N\textsubscript{2}O that is produced by agriculture that is considered an ozone-depleting practice.
Key connections made by Crutzen

- mankind can increase N\textsubscript{2}O emissions by fertilizing crops

- N\textsubscript{2}O has a long lifetime in troposphere, so can reach the stratosphere

- Increase in tropospheric N\textsubscript{2}O will increase stratospheric NO\textsubscript{x}

- Increase in NO\textsubscript{x} will result in decrease in steady state ozone

- e.g. Mankind can alter stratospheric ozone without leaving the ground!
Direct Injection of emissions from SSTs

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2 \\
\text{Net} - \text{O}_3 + \text{O} & \rightarrow \text{O}_2 + \text{O}_2
\end{align*}
\]

\[
\frac{d[O_3]}{dt} \approx -2[O](k_{O_3}[O_3] + k_{OH}[OH] + k_{NO}[NO])
\]
Richard Stolarski and Ralph Cicerone

\[
\begin{align*}
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{O} & \rightarrow \text{Cl} + \text{O}_2 \\
\text{Net} & - \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2
\end{align*}
\]

\[
\frac{d[O_3]}{dt} \approx -2[O](k_{O_3}[O_3] + k_{OH}[OH] + k_{NO}[NO] + k_{clo}[ClO])
\]
We will see in a future lecture that each of these cycles contributes to ozone loss at slightly different altitudes and in different proportions.

**FIGURE 12.8** (a) Rates of removal of O$_3$ at 38°N in May 1993 due to NO$_x$, (ClO$_x$ + BrO$_x$), and HO$_x$ chemistry, respectively, as a function of altitude in the stratosphere (adapted from Wennberg et al., 1994); (b) 24-h average rates of removal of O$_3$ as a function of altitude (adapted from Osterman et al., 1997).
Dr. James E. Lovelock, Inventor

The electron capture detector

“...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.”

Note that chlorofluorocarbons are quite stable in the troposphere because they do not absorb sunlight. They only photolyze once they are high in the stratosphere.

**FIGURE 12.14** Semilogarithmic plot of the absorption cross sections of the halogenated methanes at 298K: *, CHCl₃; ■, CHClF₂; □, CH₂Cl₂; ●, CH₂ClF; ▲, CCl₃; ◆, CCl₂F (CFC-11); ○, CCl₂F₂ (CFC-12); ▼, CCIF₃ (adapted from Hubrich and Stuhl, 1980).
Mario Molina and F. Sherwood Rowland

\[
\text{CFCl}_3 + \text{hv} \rightarrow \text{CFCl}_2 + \text{Cl} \\
\text{CF}_2\text{Cl}_2 \text{hv} \rightarrow \text{CF}_2\text{Cl} + \text{Cl}
\]

Predicted tens of percents of ozone loss

The deadly weapon!


1614 citations – even with typo!
The pieces come together!

Brewer-Dobson circulation 2

Penetration of UV radiation

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

release

Cl + O₃ → ClO + O₂
ClO + O → Cl + O₂
Net - O₃ + O → O₂ + O₂

“spark”

Cl + O₃ → ClO + O₂

“flame”

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

Net - O₃ + O → O₂ + O₂

destruction

‘un’reactivity

transport

source

“spark”

“flame”
Rowland (1974): "The work is going very well, but it may mean the end of the world."

Industry pauses while it waits for word that ozone is, in fact, being depleted – i.e., let scientists look for the smoking gun!
So, all we need is to observe ozone losses in conjunction with increases in CFCs, easy, right?

**FIGURE 12.13** Concentrations of CFC-11 and CFC-12 in air in the 30°N to 90°N region as a function of time. The different curves represent measurements made at various locations (adapted from WMO, 1995).
CFCs nearly double over 15 years!

With no observable ozone loss!

FIGURE 13.11 Percentage variations in total column ozone smoothed using a 12-month running mean for a network of stations in (a) Europe, (b) Eastern Siberia and the Far East, and (c) Western Siberia from 1973 to March 1994. The arrows show the expected QBO. In (c) the dashed line shows the component that has a periodicity expected for the QBO (adapted from Bojkov et al., 1994).
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 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!

• 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!
It doesn’t hurt your case to have a huge hole in the ozone appear right when government and the public is doubting your theories!

Sep 29 2003