Stratospheric Ozone: How We Came to Understand its Chemistry and Response to Perturbations

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A few background facts

- Ozone in atmosphere “discovered” by measurement of cutoff of solar spectrum in UV
- Ozone determined to be a layer at high altitude (in stratosphere)
- Ozone column amount quantitatively measured by UV absorption
- First ozone theory by Chapman (1930)
Ozone Photochemistry
Odd Oxygen (O atoms + O₃ molecules)

Chapman Theory 1930

Initiation: \( h\nu + O₂ \rightarrow O + O \)
\((\lambda < 240 \text{ nm})\)

Propagation: \( O + O₂ + M \rightarrow O₃ + M \)
\( h\nu + O₃ \rightarrow O₂ + O \)
\((200 \text{ nm} < \lambda < 300 \text{ nm})\)

Termination: \( O + O₃ \rightarrow O₂ + O₂ \)

Ozone is continuously being made and destroyed in the atmosphere

Sydney Chapman
But there is a lot of laboratory background that underlies Chapman’s theory of stratospheric ozone

- Laboratory ozone decomposition experiments (circa 1900-1930)
  - Ozone obtained from pure oxygen by e.g. electric discharge
  - Ozone change measured by pressure change ($2O_3 \rightarrow 3O_2$)
  - Ozone change studied as a function of:
    - Temperature
    - Visible light
    - UV light
    - Contaminant gases (i.e. water, chlorine)
Catalysis Accelerates Termination Reaction

Hydrogen oxides, Nitrogen oxides
Chlorine oxides, Bromine oxides

Example: Chlorine

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

Fritz Weigert first studied the impact of chlorine on ozone decomposition in his laboratory in \textbf{1907}.
A few of the many references to chlorine-ozone studies in the laboratory


The Nobel Prize in Chemistry 1967
Manfred Eigen, Ronald G.W. Norrish, George Porter

The Nobel Prize in Chemistry 1967 was divided, one half awarded to Manfred Eigen, the other half jointly to Ronald George Wreyford Norrish and George Porter "for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy".
How did we get involved in chlorine chemistry in the atmosphere?

Stedman, circa 1972: “Chlorine destroys ozone; everybody knows that!”
How did we come to know about the importance of CFCs?

**Article**


**Stratospheric sink for chlorofluoromethanes: chlorine atomc-atalysed destruction of ozone**

Mario J. Molina & F. S. Rowland

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**Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the Chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.**
The information was out there for people like us to have put forward the fluorocarbon-ozone theory – but we didn’t!


Jim Walker
"What about Carbon tet?"

Chuck Kolb (to me), November 1973
"Have you ever thought about Freons? They are inert in the troposphere, not soluble and don’t absorb visible light. They will get up into the stratosphere where uv will produce chlorine."

Stolarski 4/23/2012 GSFC Maniac Talk
Rowland heard a talk by Lovelock – his notes below were the basis for studies by his new post-doc, Mario Molina
The Antarctic Ozone Hole

June 1985: Farman et al. paper published
July 1985: WMO/UNEP Ozone Assessment meeting
August 1985: Bhartia presentation at IAGA
Rowland: This observation by the British brought the NASA satellite people back to look at their data. Actually, they’ve gotten sort of a bad rap about it. What they did was program their data to reject, but notify, that some unusually low ozone values were being recorded. If you are getting unexpected low values when the instrument is working at the very limit of its detection, then you put that aside, saying, maybe there is something happening there that is real, but maybe it is an instrumental problem, and we’ll have to go back and look at it carefully.

http://WWW.EOEARTH.ORG/ARTICLE/CFC-OZONE PUZZLE: _LECTURE?TOPIC=49594
Figures from our 1986 Nature paper on the ozone hole

Nimbus 7 satellite measurements of the springtime Antarctic ozone decrease


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What about the theory of the ozone hole?

Stolarski 4/23/2012 GSFC Maniac Talk
Feldafing Workshop, June 1984

The rationale for the scope of the present assessment report was based on information gained at a scientific workshop, entitled "Current Issues in Our Understanding of the Stratosphere and the Future of the Ozone Layer" which was held in Feldafing, Federal Republic of Germany in June 1984 with international participation, co-sponsored by NASA, FAA, WMO, and BMFT.

Sherry Rowland: “Missing Chemistry”

– Don’t need to worry about fast channels
– What if one reservoir molecule reacted with another, e.g. ClONO$_2$ and HCl?
– Molina (and Sato and Rowland independently) had been studying this reaction in the lab
– They found a small, but measureable rate coefficient
– Inserted into a model, the reaction implied that 30% of the global amount of ozone should have already disappeared
– Later reported that reaction was occurring on teflon walls of the experiment
Chlorine Photochemistry (normal)

- Active Chlorine < 0.5%
- Chlorine Reservoirs

Diagram:
- Cl
- ClO
- HCl
- ClNO₃

Stolarski 4/23/2012 GSFC Maniac Talk
Polar Stratospheric Clouds (PSCs)

Fig. 1. Saturation mixing ratios of water vapor with respect to ice (in ppm, i.e. units of $10^{-6}$ g H$_2$O/g air) vs pressure for Maudheim base (70°03′ S, 10°56′ W) during the 1950 Antarctic winter. The curves extend up to the bursting level of the balloons. The temperature data used were half-monthly means. The position of the half-monthly mean tropopause is indicated. The approximate dates over which “Stratospheric Cist” were reported are also indicated.

On the nature of persistent stratospheric clouds in the Antarctic

By JOHN L. STANFORD, Physics Department, Iowa State University, Ames, Iowa 50011, U.S.A.

(Manuscript received November 8, 1976; in final form January 26, 1977)

ABSTRACT

Thin, persistent very high clouds called “Stratospheric Cist” were reported at Maudheim base (71°03′ S, 10°56′ W) during the 1950-51 austral winters. The nature of these clouds, whether they are H$_2$O or dust, is of importance in the proposed sink for stratospheric moisture in the Antarctic winter.

Results are presented from analyses of unpublished daily cloud reports and daily upper air measurements from the Maudheim expedition. The results reveal strong evidence that the “Stratospheric Cist” were stratospheric ice clouds. Given this identification, an upper limit of 6-7 ppm can be assigned to the water vapor mixing ratio in the lower stratosphere for the 1950-51 Antarctic winters.

A Model of the Antarctic Sink for Stratospheric Water Vapor

Anne R. Douglass and John L. Stanford

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Model calculations have been performed to quantitatively estimate the amount of stratospheric H$_2$O removed by freeze out during the winter in the Antarctic region. The model uses realistic temperature and wind fields based on Hartmann’s Nimbus 5 temperature grids. For the 1973 Antarctic winter stratosphere, initial water vapor mixing ratios of 2.7 and 3.0 ppm lead to removal of 1.6 and 2.7 x 10$^{10}$ kg H$_2$O from the lower stratosphere. This annual sink magnitude is small, representing about 2% of the total stratospheric H$_2$O burden and about 10% of the apparent sink identified by Ellissesser (1974).

However, a sink of this magnitude is close to the lower rate estimates of water produced in the stratosphere by methane oxidation. The sink is not large enough to balance additional, proposed water vapor sources.
Chlorine Photochemistry (polar)

Active Chlorine Increases By 50 to 100x

PSC Reactions Drain Chlorine Reservoirs
Variety of Initial Theories of the Ozone Hole

- Chlorine chemistry

- Dynamics – was ozone just moved around by wave motions but conserved over the entire polar region? No, there was a net decrease.

- Solar Cycle – NOx chemistry variations induced by solar cycle- required N2O change that was not observed.

- Other?
“Smoking Gun Slide”

From: NRC “Ozone Depletion, Greenhouse Gases, and Climate Change” (Anderson et al., 1989)

Stolarski 4/23/2012 GSFC Maniac Talk
There were alternative theories
An aside on giving talks on hot issues such as the fluorocarbon-ozone issue was at one time

- You are an expert on science: separate your science from any opinions on what should be done by society

- There are no dumb questions: Even if you have heard a question a thousand times respect the questioner

- Be prepared: you know the standard questions so you should have a prepared approach to these

- If you don’t know the answer say so.
Question asked over and over when making presentations on fluorocarbon-ozone theory:
Fluorocarbons are heavier than air—how can they get to the stratosphere?

Diffusive Separation in the Thermosphere: a concept studied since the 1960s:
graphs redrawn from Hedin and Nier (1965)
Final thoughts

• Details are important, but if you don’t try to step back and see the big picture you can waste a lot of time on the wrong details

• Opportunities abound: will you recognize them? Will you follow up on them? Or will you just let them pass by?

• Ideas are cheap – Selection of good ones and follow through on them is what counts.
Quotes

• Committee: A cul-de-sac to which ideas are lured and then quietly strangled. -- John A. Lincoln

• Man will occasionally stumble over the truth but most of the time he will pick himself up and continue on. -- W. S. Churchill

• Don't worry about people stealing your ideas. If your ideas are any good, you'll have to ram them down people's throats. -- unknown

• A complex system that works is invariably found to have evolved from a simple system that worked ...A complex system designed from scratch never works and cannot be patched up to make it work. You have to start over, beginning with a working simple system. -- Grady Booch