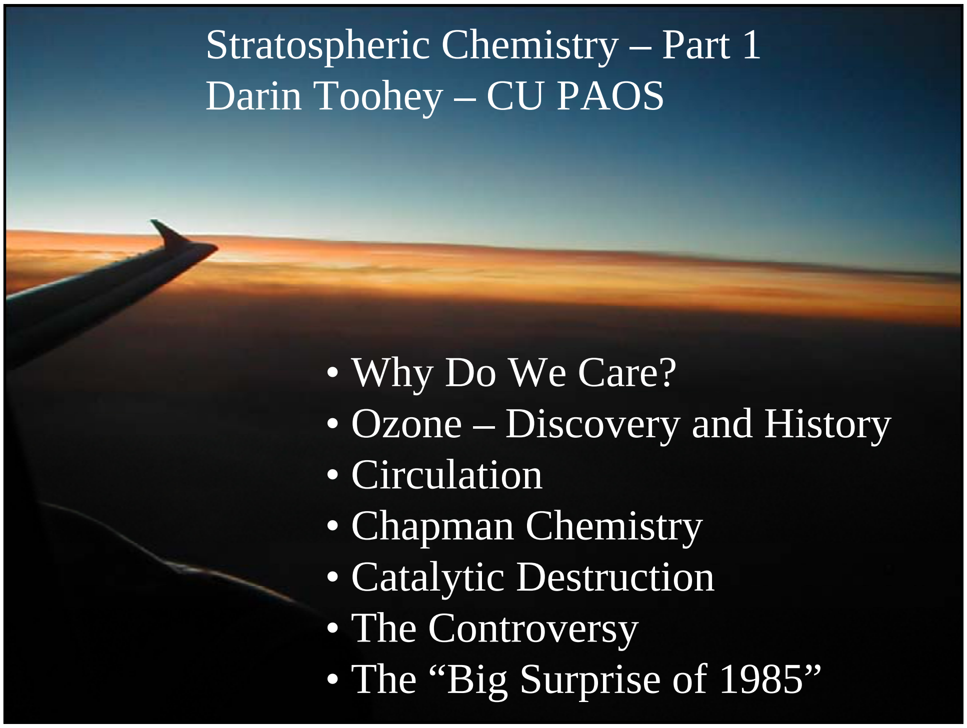


Some resources that I borrowed from

http://web.lemoyne.edu/~giunta/chapman.html

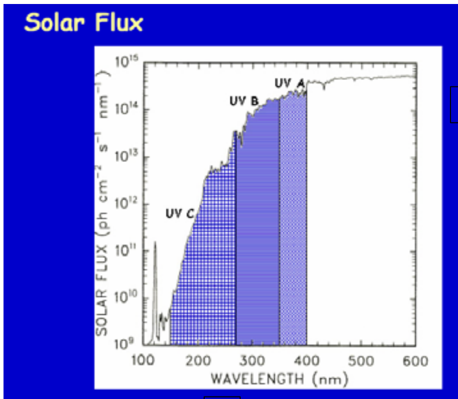
http://www.wv-hsta.org/uvproje/history.htm

http://remus.jpl.nasa.gov/milestones.ht
m

http://www.smcm.edu/users/cmmattia/leadership/ozone/Assets/Timeline/timeline2.htm

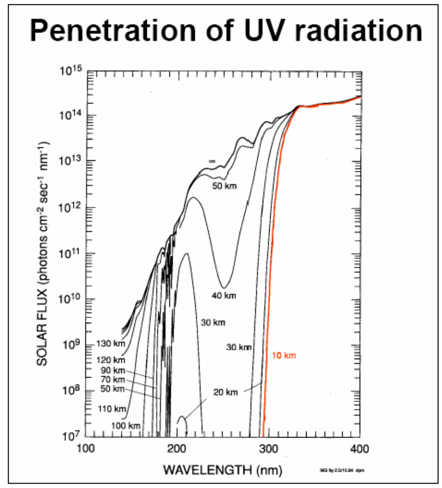
http://www.ciesin.org/docs/011-464/011-464.html

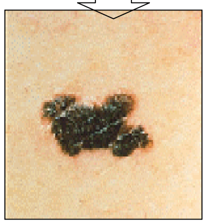
http://www.nrdc.org/air/pollution/hozone.asp



Why do we care?

Phytoplankton





Melanoma

The Human Connection

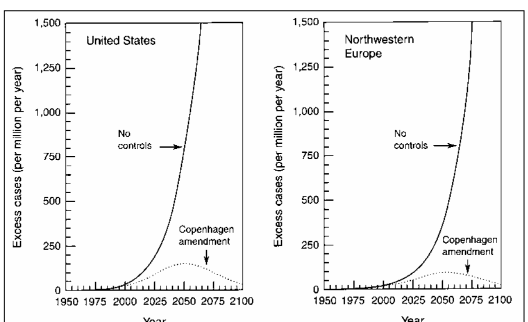


FIGURE 13.20 Estimated excess cases of skin cancer in the United States and northwestern Europe if no controls had been imposed on CFCs and halons and those under the Copenhagen Amendment (adapted from Slaper *et al.*, 1996).

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)

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

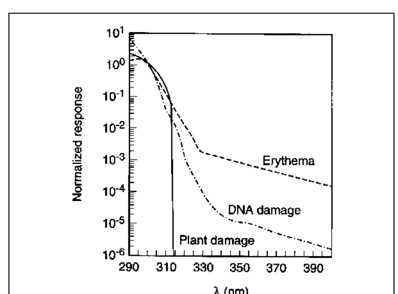


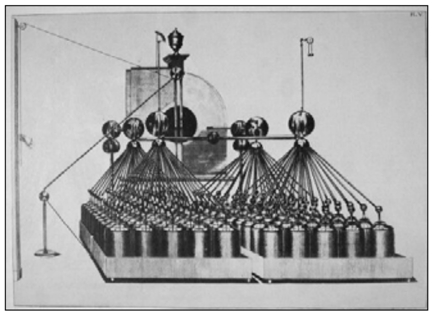
FIGURE 13.15 Normalized action spectra taking response = 1.0 at 300 nm (adapted from Madronich, 1992).

Ozone History

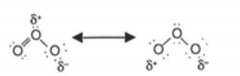
Martinus Van Marum 1826

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 a component of air!

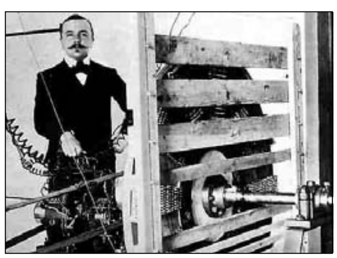


Christian Friedrich Schönbein, 1799-1868



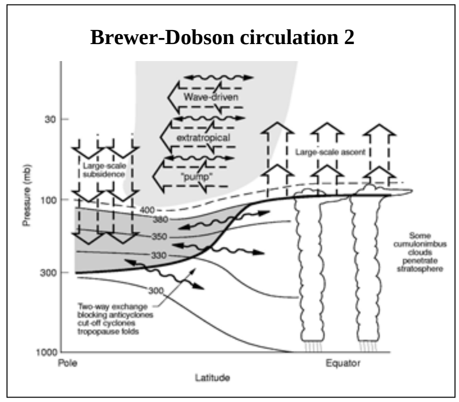
Officially named as a chemical in 1840 by Christian Schönbein, after he noted that it had a smell that was similar to that of phosphorus when exposed to air

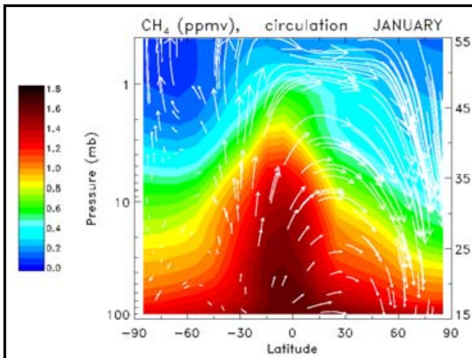
It was soon realized that ozone was a good disinfectant. Otto was first to market a water purifier based on ozone

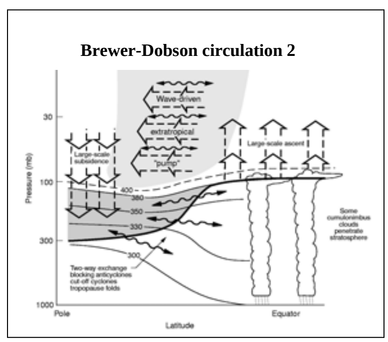


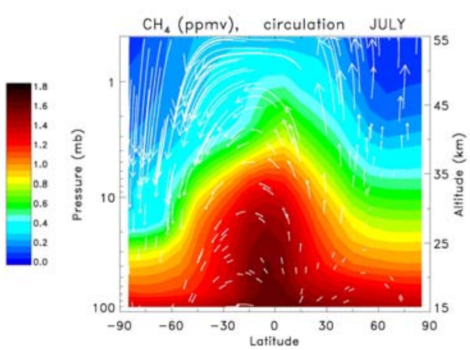
Marius Paul Otto

In 1923, Gordon Dobson developed the first spectrometer to measure ozone in the atmosphere, and he characterized its latitudinal seasonal variability









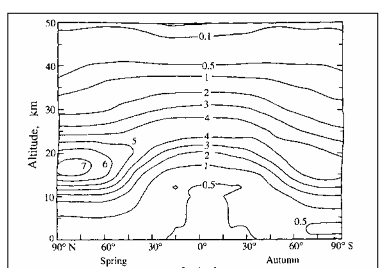
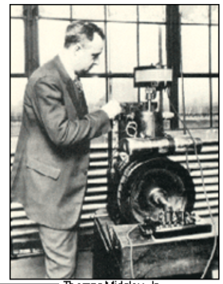


FIGURE 4.4 Zonally averaged ozone concentrations (in units of 10^{12} molecules cm^{-3}) as a function of altitude, March 22 (Johnston, 1975). Ozone concentration at the equator peaks at an altitude of about 25 km. Over the poles the location of the maximum is between 15 and 20 km. At altitudes above the ozone bulge, O_3 formation is oxygen-limited; below the bulge, O_3 formation is photon-limited.

1928 – Thomas Midgley develops chlorofluorcarbons for DuPont, inhaling them to prove that they nontoxic. These non-flammable compounds soon replace the deadly compounds (such as ammonia and SO_2) in home refrigerators



Thomas Midgley, Jr.

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!

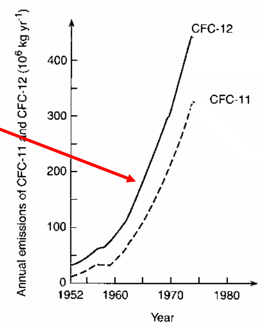


FIGURE 12.11 Estimated annual worldwide releases of CFC-11 and CFC-12 from 1952 to 1980. Data from Chemical Manufacturers' Association (adapted from National Research Council, 1984).

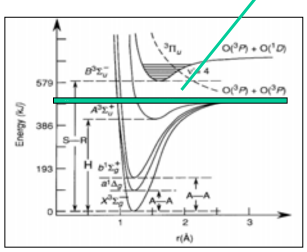
In 1930, Sydney Chapman published several theoretical papers on upper-atmospheric ozone – now known as the "Chapman Cycle"

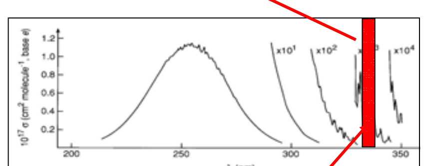
$$O_2 + h\nu \rightarrow O + O \quad (\lambda < 242\text{ nm}) \quad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (2)$$

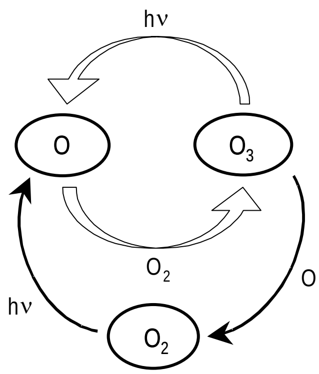
$$O_3 + h\nu \rightarrow O_2 + O \quad (\lambda < 336\text{ nm}) \quad (3)$$

$$O_3 + O \rightarrow O_2 + O_2 \quad (4)$$





10^{-21}



rate 1 = J_{O2} [O_2] ($J_{O2} \approx 10^{-11}$ s^{-1}, 30 km)

rate 2 = k_2[O][O_2][M] ($k_2 \approx 9\times10^{-34}$ cm^6s^{-1} at 250 K)

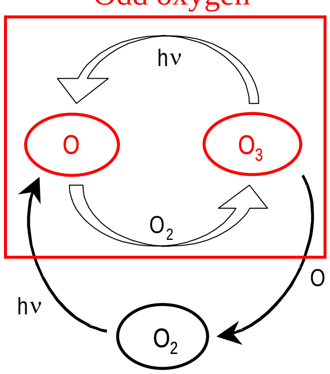
rate 3 = J_{O3} [O_3] ($J_{O3} \approx 10^{-3}$ s^{-1} at 30 km)

rate 4 = k_4[O][O_3] ($k_4 \approx 2\times10^{-15}$ cm^3s^{-1} at 250 K)

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

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

"Odd oxygen"



Rate 1 = J_{O2} [O_2]

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

Rate 3 = J_{O3} [O_3]

Rate 4 = k_4[O][O_3]

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

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

(note, you get the same by assuming O_2 is in steady state)

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

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

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

$$\boxed{[O_3] = 0.21\left(\frac{k_2}{k_4}\right)^{\frac{1}{2}}\left(\frac{J_{O_2}}{J_{O_3}}\right)^{\frac{1}{2}}[M]^{\frac{3}{2}}}$$

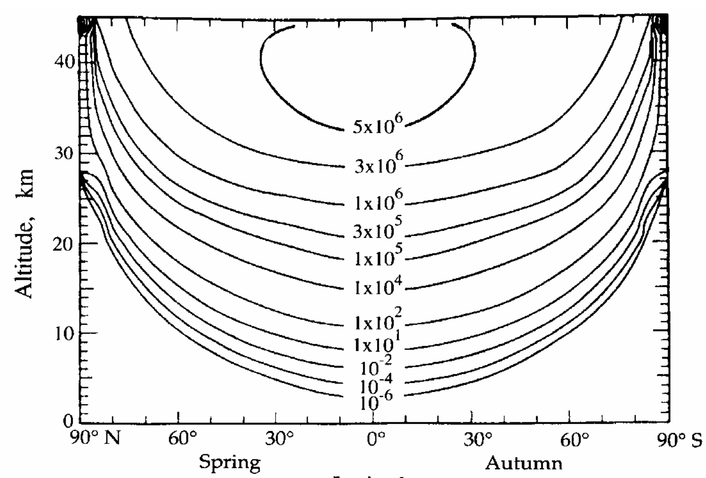


FIGURE 4.3 Zonally averaged rate of ozone formation (molecules cm^{-3} s^{-1}) from the photolysis of O_2 (Johnston, 1975).

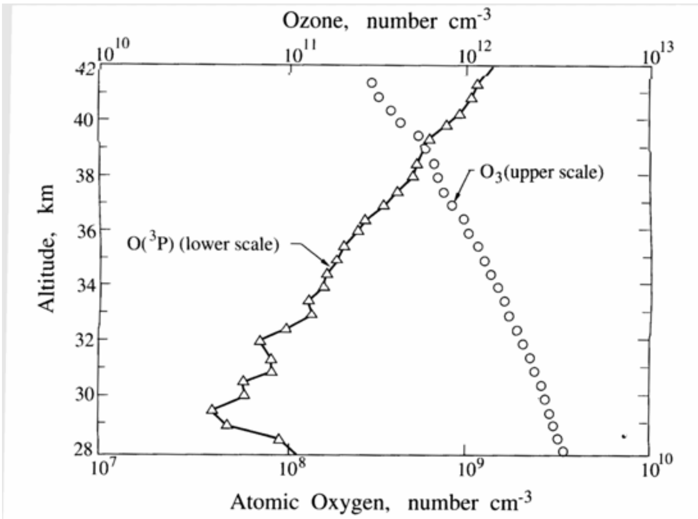


FIGURE 4.2 Concentrations of atomic oxygen and ozone measured simultaneously as a function of altitude on December 2, 1977 at Palestine, Texas (32° N). Solar zenith angle θ_0 = 50° (World Meteorological Organization, 1981). Note different scales for the concentrations of the two species.

Problem – Chapman mechanism predicts more ozone than what is observed!

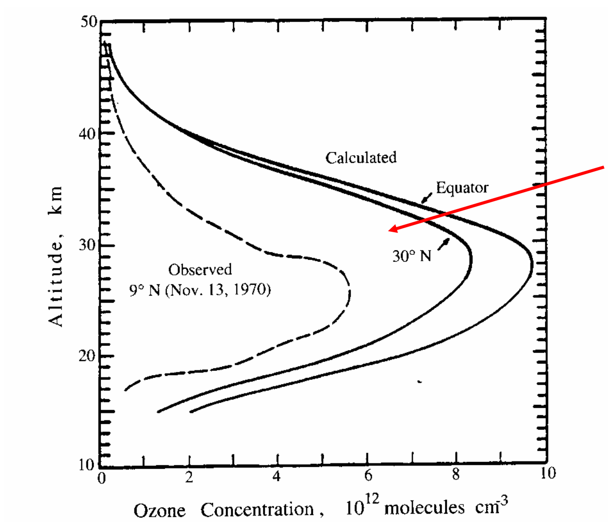


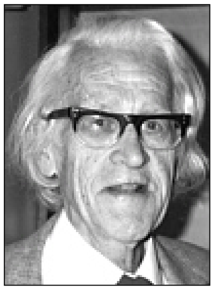
FIGURE 4.6 Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9° N) on November 13, 1970.

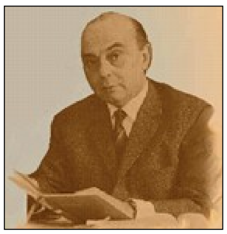
What's missing?

Faster

$$O_3 + O \rightarrow O_2 + O_2$$

http://www.accessexcellence.org/WN/SUA06/nobchem.html





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

$H + O_3 \rightarrow OH + O_2$

$\underline{OH + O \rightarrow H + O_2}$

Net - $O_3 + O \rightarrow O_2 + O_2$

Bates, D.R. and M. Nicolet, The Photochemistry of the Atmospheric Water Vapor, J. Geophys. Res., 55, 301, 1950

Catalysis

$H + O_3 \rightarrow OH + O_2$ rate = $k_a[H][O_3]$

$\underline{OH + O \rightarrow H + O_2}$ rate = $k_b[OH][O]$

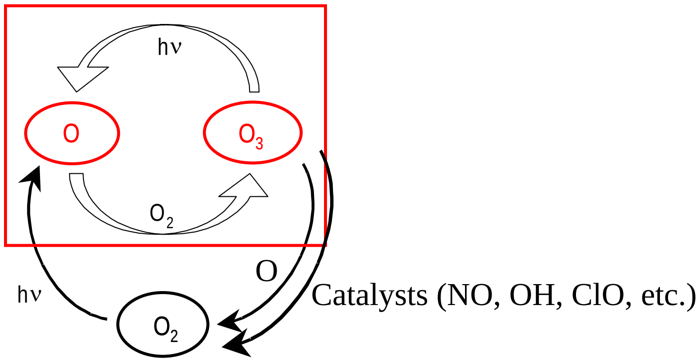
Net - $O_3 + O \rightarrow O_2 + O_2$

$$\frac{d[O_3]}{dt} \approx -2k_4[O][O_3] - 2k_b[OH][O]$$

Replace k_4 $[O][O_3]$ with apparent loss

$$k_4^{app} = k_4\left[1 + \frac{k_b[OH]}{k_4[O_3]}\right] \qquad [O_3] = 0.21^2\left(\frac{k_2}{k_4^{app}}\right)^{\frac{1}{2}}\left(\frac{J_{O_2}}{J_{O_3}}\right)^{\frac{1}{2}}[M]^{\frac{3}{2}}$$

$> k_4$



Production stays the same (it's due to photolysis of O_2)
Loss increases

1970 - Paul Crutzen proposes that NO_x from bacterial N_2O can participate in atmospheric chemistry as NO formed in the stratosphere

$$\boxed{N_2O + O(^1D) \rightarrow NO + NO}$$

"Influence of Nitrogen Oxides on Atmospheric Ozone Content"
Quarterly Journal of the Royal Meteorological Society 96 (1970):320.

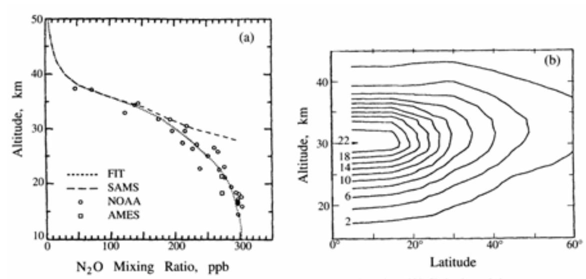


FIGURE 4.7 (a) Vertical profiles of N_2O over the tropics at equinox circa 1980. Circles denote balloon-borne measurements at 9° N and 5° S; squares represent aircraft measurements between 1.6° S and 9.9° N. Dashed curve refers to the average of satellite measurements at 5° N, equinox, between 1979 and 1981. This compilation of data was presented by Minschwaner et al. (1993), where the original sources of data can be found. The dotted curve indicates the vertical profile used by Minschwaner et al. to estimate the lifetime of N_2O. (b) Calculated diurnally averaged loss rate for N_2O (in units of 10^{12} molecules cm^{-3} s^{-1}) as a function of altitude and latitude, at equinox. The loss rate includes both photolysis and reaction with $O(^1D)$ (Minschwaner et al, 1993).

Formation of NO

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ — J_{O3}

$O(^1D) + N_2/O_2 \rightarrow O(^3P) + N_2/O_2$ — ~ gas kinetic

$N_2O + h\nu \rightarrow N_2 + O(^1D)$ — J_{N2O}

$N_2O + O(^1D) \rightarrow N_2 + O_2$ — $k_{2a} = 5 \times 10^{-11}$ cm^3 s^{-1}

$\rightarrow NO + NO$ — $k_{2b} = 6.7 \times 10^{-11}$ cm^3 s^{-1}

$$Yield = \frac{2k_{2b}[O(^1D)]}{\{k_{2b}+k_{2a}\}[O(^1D)] + J_{N_2O}}$$

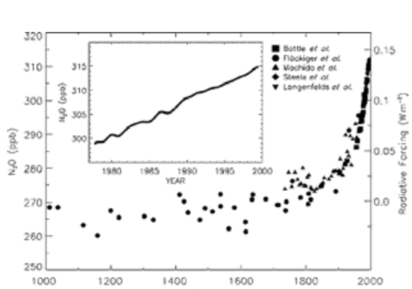
Production of NO

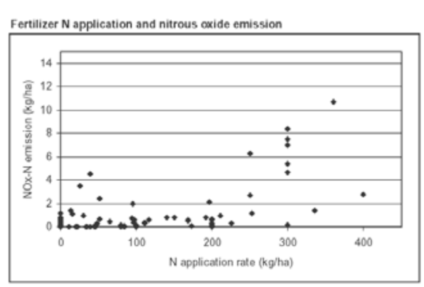
Loss of N_2O

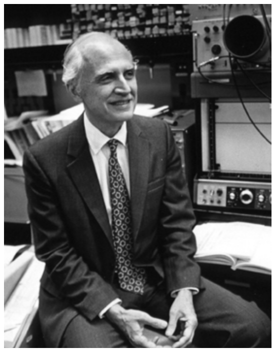
~3.5-4.0% of the N_2O becomes NO_y

Key connections made by Crutzen

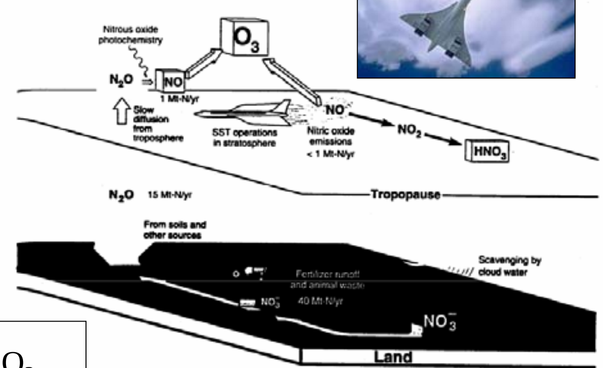
- mankind can increase N_2O emissions by fertilizing crops
- N_2O has a long lifetime in troposphere, so can reach the stratosphere
- Increase in tropospheric N_2O will increase stratospheric NO_x
- Increase in NO_x will result in decrease in steady state ozone
- e.g. **Mankind can alter stratospheric ozone without leaving the ground!**







Harold Johnston

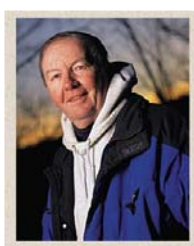


$NO + O_3 \rightarrow NO_2 + O_2$

$\underline{NO_2 + O \rightarrow NO + O_2}$

Net - $O_3 + O \rightarrow O_2 + O_2$

$$\frac{d[O_3]}{dt} \approx -2[O]\left(k_{O_3}[O_3] + k_{OH}[OH] + k_{NO}[NO]\right)$$



Richard Stolarski and Ralph Cicerone

$Cl + O_3 \rightarrow ClO + O_2$

$\underline{ClO + O \rightarrow Cl + O_2}$

Net - $O_3 + O \rightarrow O_2 + O_2$

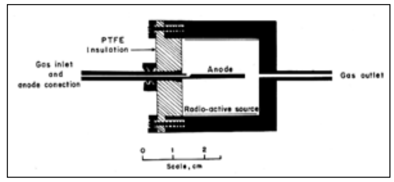
Stratospheric Chlorine: A Possible Sink for Ozone, Can. J. Chem., 52, 1610-1615, 1974

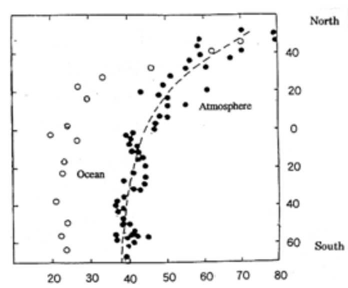
$$\frac{d[O_3]}{dt} \approx -2[O]\left(k_{O_3}[O_3] + k_{OH}[OH] + k_{NO}[NO] + k_{clo}[ClO]\right)$$

(also McElroy and Wofsy, but more on them in Part 2)

Dr. James E. Lovelock, Inventor

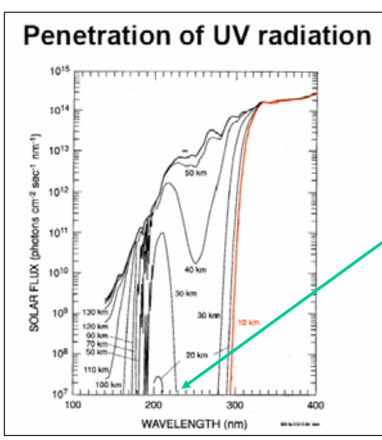
The electron capture detector





"…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."

Distribution of CCl_3F in and over the North and South Atlantic Ocean, Nature, Vol. 241, January 19, 1973



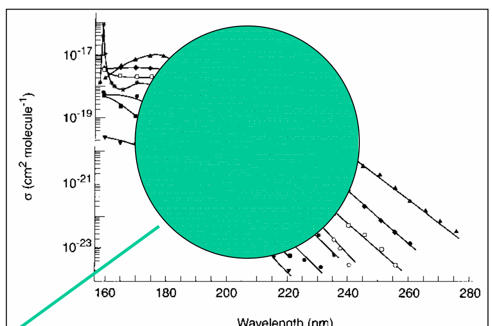


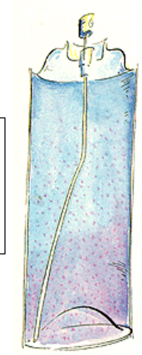
FIGURE 12.14 Semilogarithmic plot of the absorption cross sections of the halogenated methanes at 298K: +, $CHCl_3$; ■, $CHClF_2$; □, CH_2Cl_2; ●, CH_3ClF; ▲, CCl_4; ♦, CCl_3F (CFC-11); ○, CCl_2F_2 (CFC-12); ▼, $CClF_3$ (adapted from Hubrich and Stuhl, 1980).

Mario Molina and F. Sherwood Rowland


Mario Molina and F. Sherwood Rowland

$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$

$CF_2Cl_2\ h\nu \rightarrow CF_2Cl + Cl$



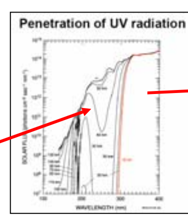
Predicted tens of percents of ozone loss

The deadly weapon!

M. J. Molina and F. S. Rowland "Stratospheric Sink for Chlorofluoromethanes: Chlorine atomic-atalysed destruction of ozone," *Nature* 249 (28 June 1974):810

1614 citations – even with typo!

The pieces come together!

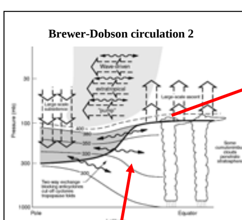


"spark"

$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$

$CF_2Cl_2\ h\nu \rightarrow CF_2Cl + Cl$

release



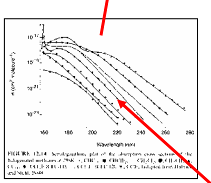
transport

$Cl + O_3 \rightarrow ClO + O_2$

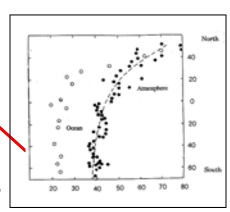
$\underline{ClO + O \rightarrow Cl + O_2}$

Net - $O_3 + O \rightarrow O_2 + O_2$

"flame"



'un'reactivity



source

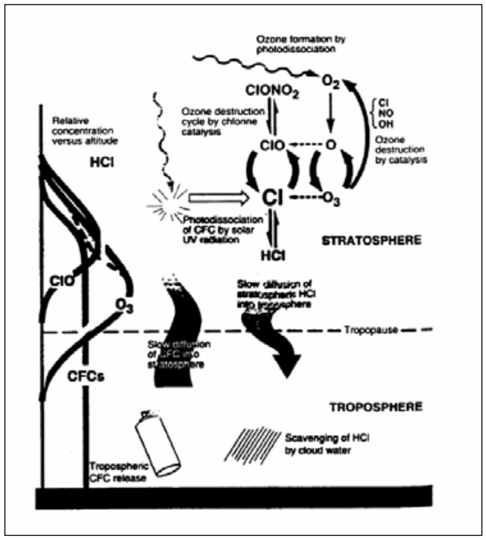
$O_2 + h\upsilon \rightarrow O + O$

$O + O_2 + M \rightarrow O_3 + M$

$O_3 + h\upsilon \rightarrow O_2 + O$

$O_3 + O \rightarrow O_2 + O_2$

destruction



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

x10!

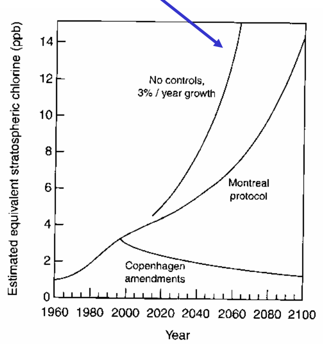


FIGURE 13.1 Estimated equivalent effective stratospheric chlorine for a continued 3% growth per year, for controls contained in the Montreal Protocol, and for those in the Copenhagen amendments (adapted from World Meteorological Organization, 1995).

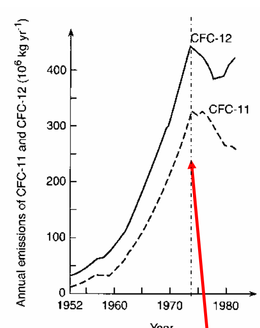


FIGURE 12.11 Estimated annual worldwide releases of CFC-11 and CFC-12 from 1952 to 1980. Data from Chemical Manufacturers' Association (adapted from National Research Council, 1984).

Spray cans banned/voluntarily boycotted

A field is born! All we need to do is to observe ozone losses in conjunction with increases in CFCs

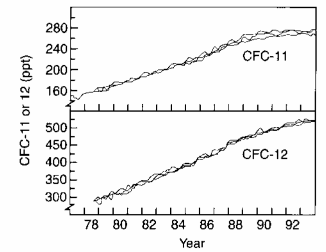
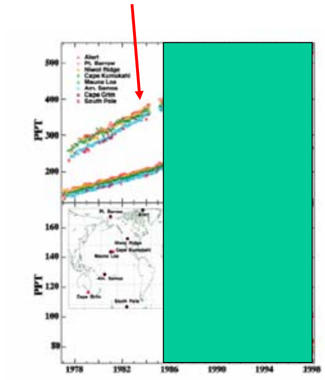


FIGURE 12.13 Concentrations of CFC-11 and CFC-12 in air in the 30°N to 90°N region as a function of time. The different curves represent measurements made at various locations (adapted from WMO, 1995).

Easy!?

Or Not?

CFCs nearly double!



But no ozone loss!

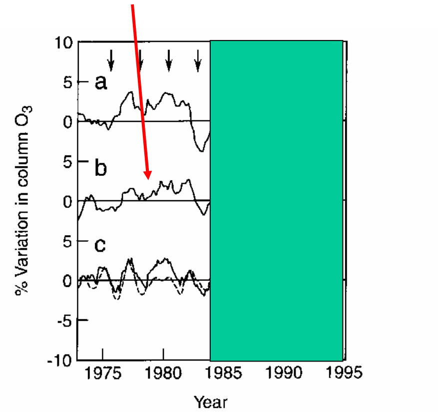


FIGURE 13.11 Percentage variations in total column ozone smoothed using a 12-month running mean for a network of stations in (a) Europe, (b) Eastern Siberia and the Far East, and (c) Western Siberia from 1973 to March 1994. The arrows show the expected QBO. In (c) the dashed line shows the component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

What really goes on?

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

Couples ClO_x to NO_x

$ClO + NO \rightarrow Cl + NO_2$

$ClO + NO_2 + M \rightarrow ClNO_3$

$ClNO_3 + h\nu \rightarrow Cl + NO_3$

$\rightarrow ClO + NO_2$

Couples ClO_x to HO_x

$Cl + HO_2 \rightarrow HCl + O_2$

$Cl + CH_4 \rightarrow HCl + CH_3$

$ClO + OH \rightarrow HCl + CH_3$

$\rightarrow Cl + HO_2$

$HCl + OH \rightarrow H_2O + Cl$

$ClO + HO_2 \rightarrow HOCl + O_2$

$HOCl + h\nu \rightarrow Cl + OH$

And NO_x is coupled to HO_x!

$OH + O_3 \rightarrow HO_2 + O_2$

$OH + O \rightarrow O_2 + H$

$OH + CO \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + O \rightarrow OH + O_2$

$HO_2 + O_3 \rightarrow OH + 2O_2$

$OH + HO_2 \rightarrow H_2O + O_2$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

Couples HO_x to NO_x

$HO_2 + NO \rightarrow NO_2 + OH$

$OH + NO_2 + M \rightarrow HNO_3 + M$

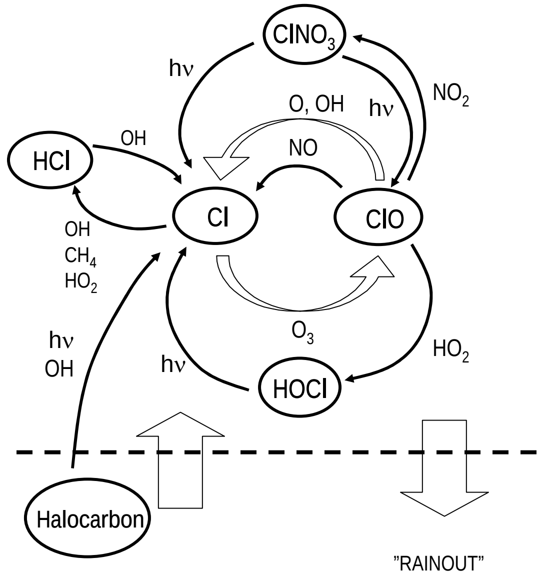
$HNO_3 + OH \rightarrow H_2O + NO_3$

$HNO_3 + h\nu \rightarrow OH + NO_2$

$HO_2 + NO_2 \rightarrow HO_2NO_2 + M$

$HO_2NO_2 + h\nu \rightarrow OH + NO_3$

+ halogen reactions…



Build a "model"

1. Source gas
2. Release of radical
3. Catalytic cycle
4. Rate determining step
5. Short-lived reserviors
6. Long-lived reserviors
7. Removal

How the radical families contribute to ozone loss

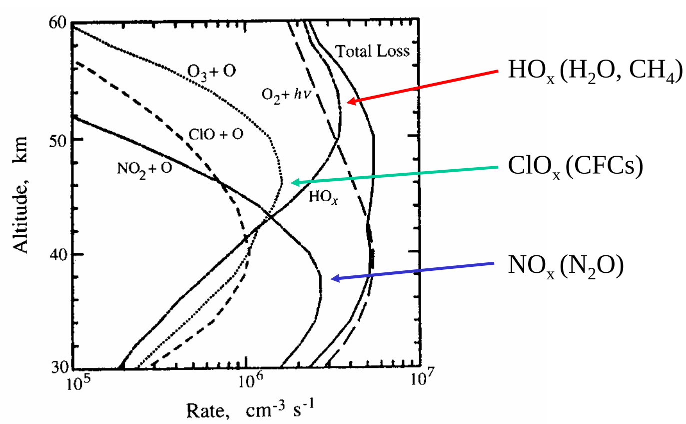


FIGURE 4.12 Diurnally averaged rates of production and loss of odd oxygen in the upper stratosphere (>30 km) calculated with a photochemical model for conditions of the ATMOS measurements at 30° N, May 1 (Minschwaner et al., 1993). Model calculations were constrained by measured profiles for O_3, H_2O, and CH_4. Photolysis of O_2 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.

Meanwhile, scientists refine their understanding

But Industry is ready, and they come our firing!

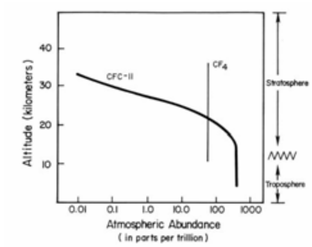
CFCs are heavier than air, and don't rise to the stratosphere – they sink!

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!



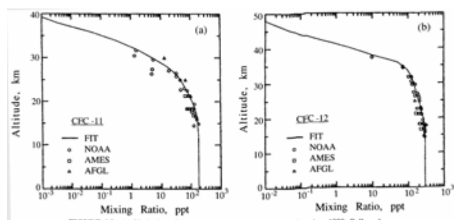
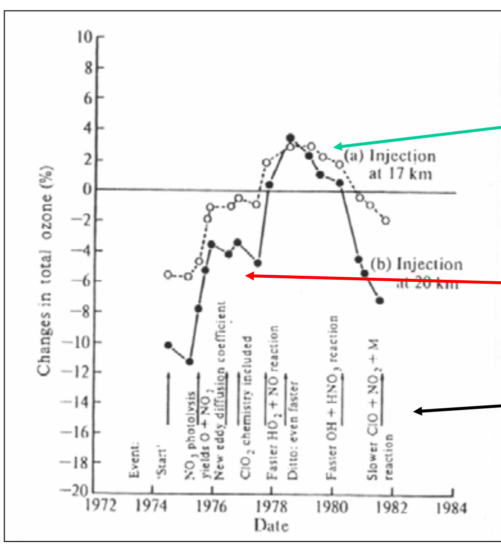


FIGURE 4.8 (a) Vertical profiles for $CFCl_3$ (CFC-11) in the tropics circa 1980. Balloon-borne measurements at 9° N and 5° S (1980) and 9° N (1983) are denoted by circles and triangles, respectively; squares represent aircraft measurements between 1.6° S and 9.9° N. This compilation of data was presented by Minschwaner et al. (1993). The solid curve is the vertical profile used by the authors in calculating the lifetime of $CFCl_3$ (b) Vertical profiles of CF_2Cl_2 (CFC-12) in the tropics circa 1980. Same as part (a).

Which one is it?
The SST story evolves…



SSTs make ozone (smog chemistry)

SSTs destroy ozone

Those darned lab chemists

The World Breathes a Sign of Relief…
In the form of CFCs

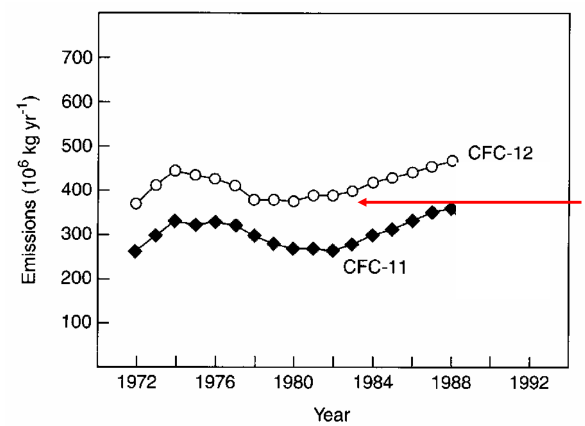
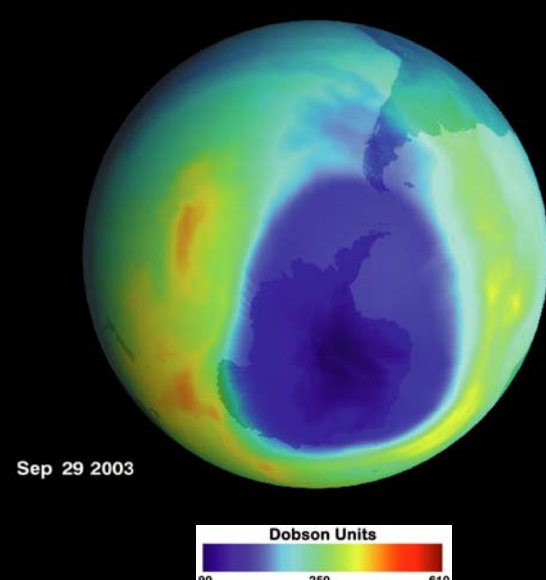


FIGURE 12.12 Estimated global annual emissions of CFC-11 and CFC-12 (adapted from World Meteorological Organization, 1995).

CFC production back on the rise!

The Big Surprise of 1985!



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!