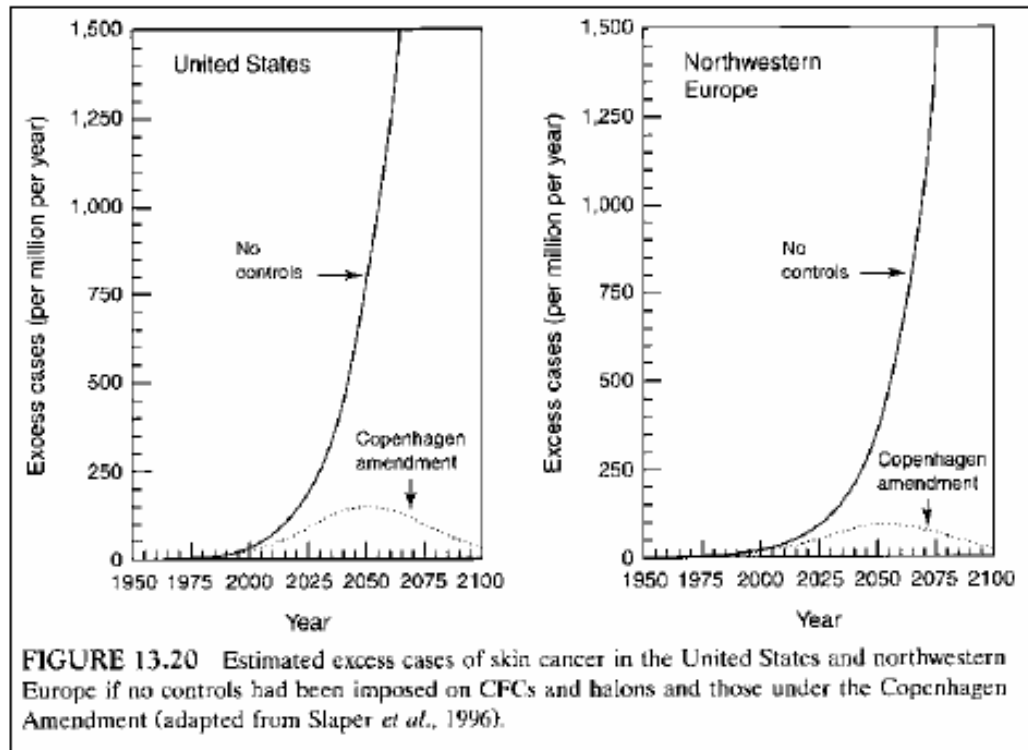


A photograph of an airplane wing against a sunset sky. The wing is on the left side, and the sky transitions from a deep blue at the top to a bright orange and yellow near the horizon. The horizon line is slightly curved, suggesting the curvature of the Earth.

Tuesday, February 8, 2011  
Chemical Cycles  
Part 1 - Stratospheric Chemistry

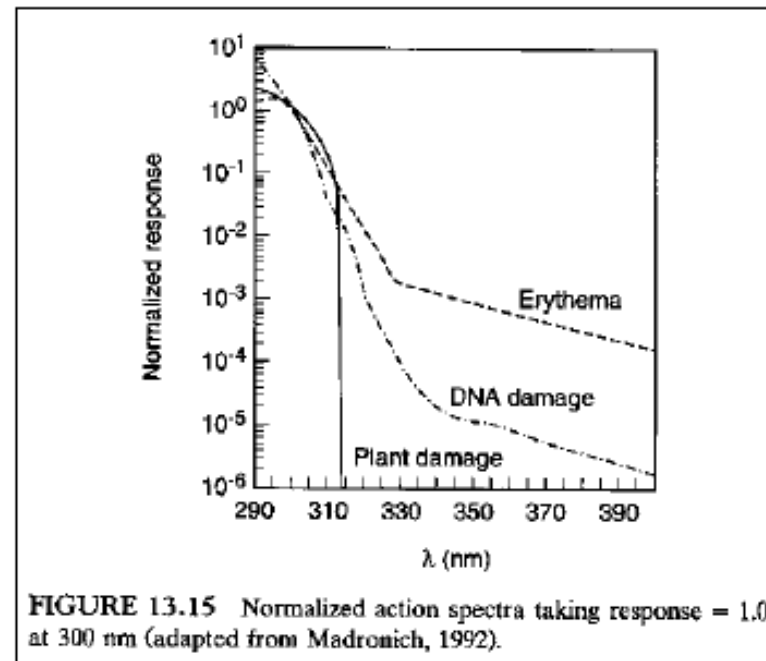
- Ozone – Discovery and history
- The stratosphere and circulation
- Chapman chemistry
- Catalysts
- The controversy
- The “ozone hole”
- International regulations

## The Human Connection



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

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](http://thinkquest.org))



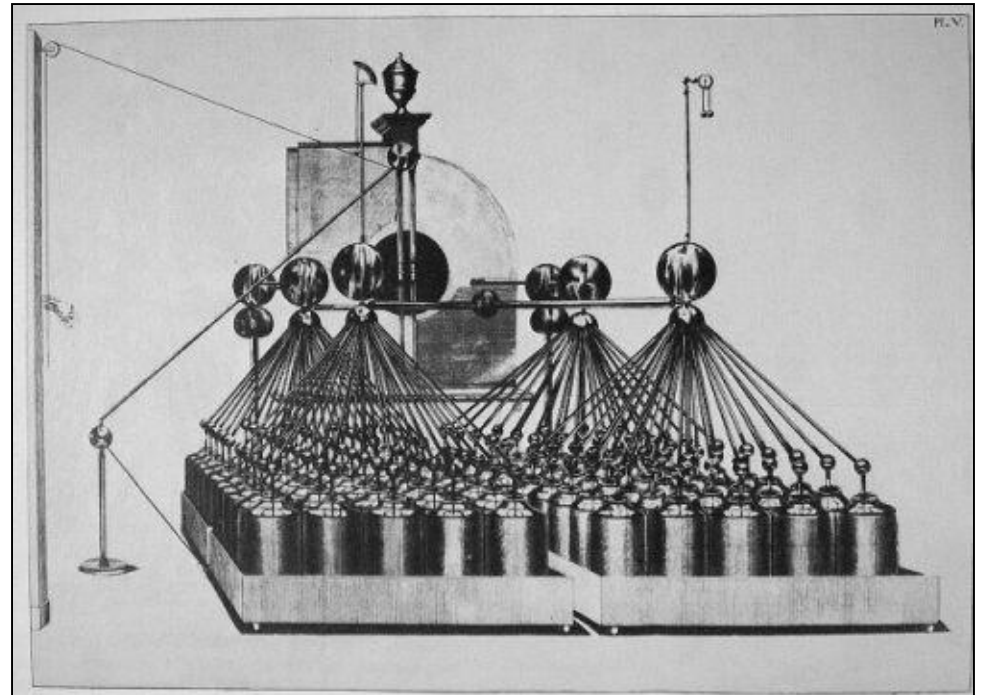
# Ozone History



*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 even a component of air!

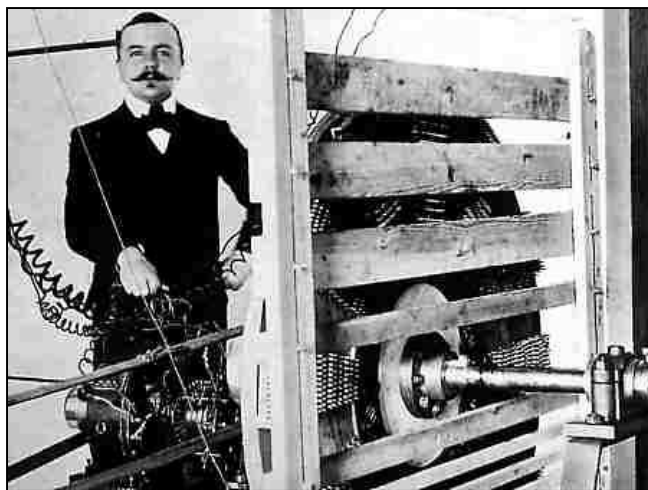
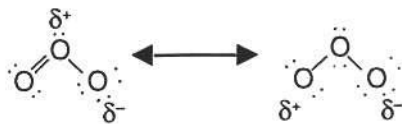




Christian Friedrich Schönbein, 1799-1868

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 (Greek “ozein” for “to smell”)

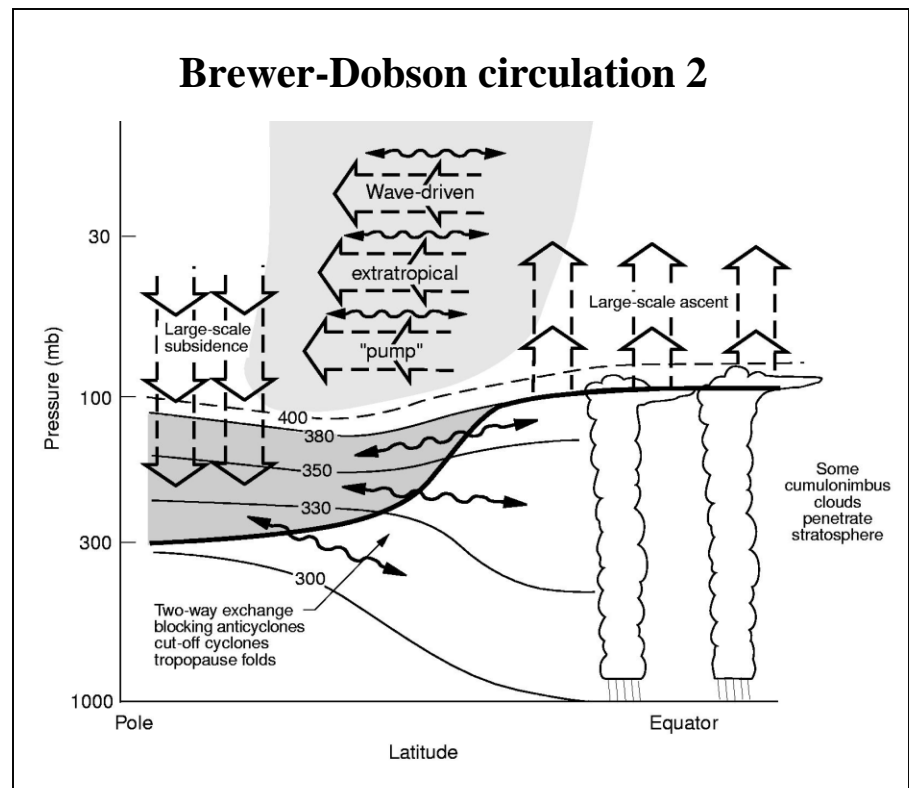
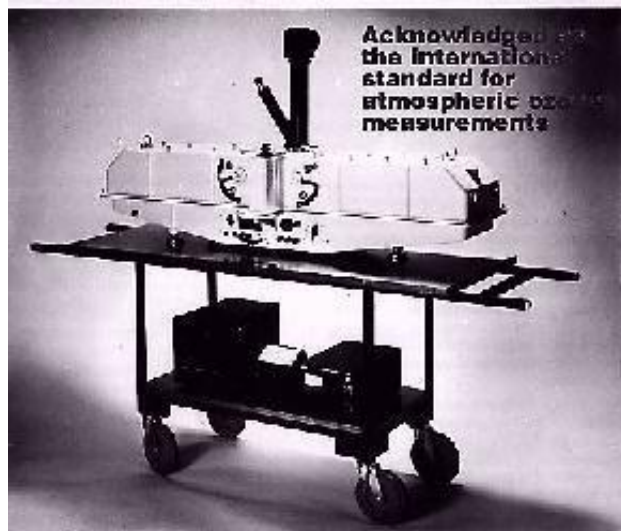
It was soon realized that ozone was a good disinfectant. Marius Paul Otto was first to market a water purifier based on ozone – in the 1800s!



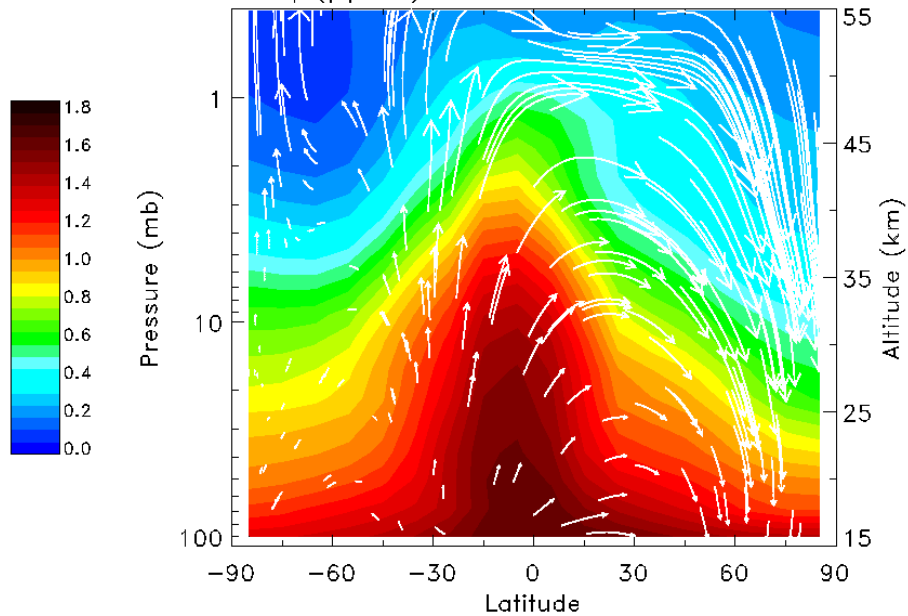
*Marius Paul Otto*



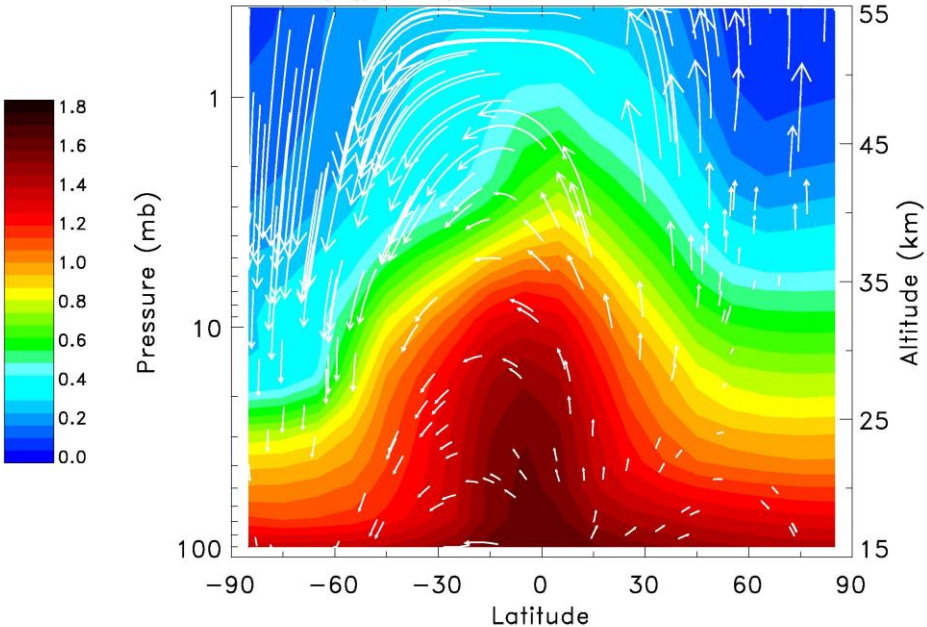
In 1923, Gordon Dobson developed the first spectrometer to measure ozone in the atmosphere, and he characterized its latitudinal seasonal variability. He shares credit for discovering that circulation of the stratosphere starts in the tropics and moves poleward.



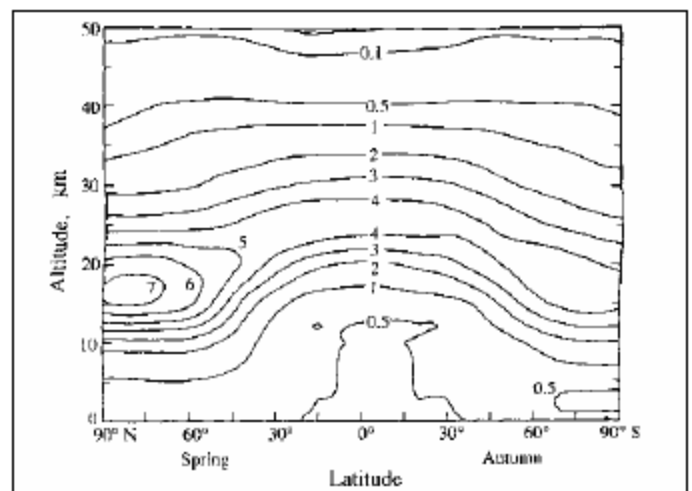
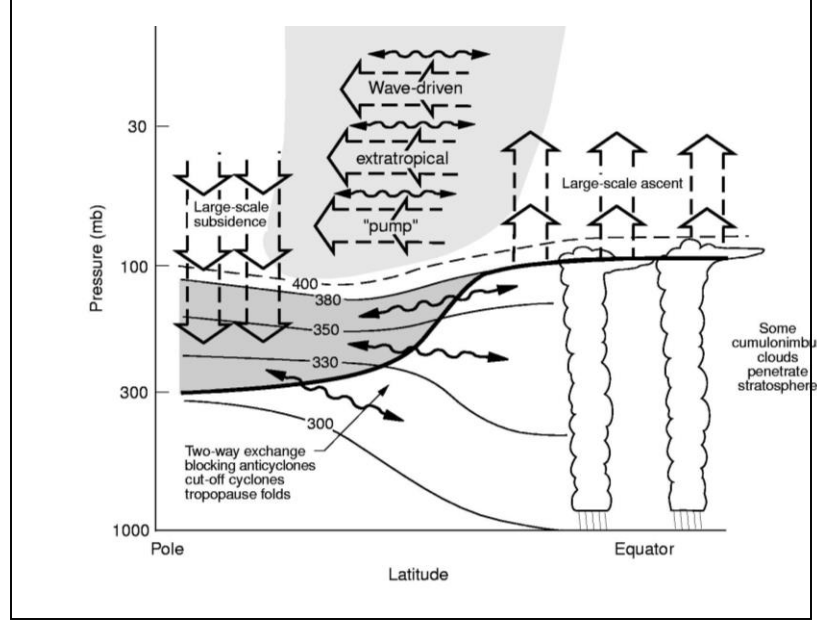
CH<sub>4</sub> (ppmv), circulation JANUARY



CH<sub>4</sub> (ppmv), circulation JULY



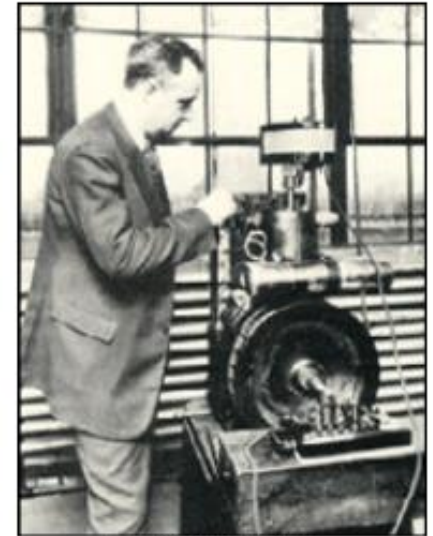
### Brewer-Dobson circulation 2



**FIGURE 4.4** Zonally averaged ozone concentrations (in units of  $10^{17}$  molecules  $\text{cm}^{-3}$ ) as a function of altitude, March 22 (Johnson, 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<sub>3</sub> formation is oxygen-limited; below the bulge, O<sub>3</sub> formation is photon-limited.



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  $\text{SO}_2$ ) 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!

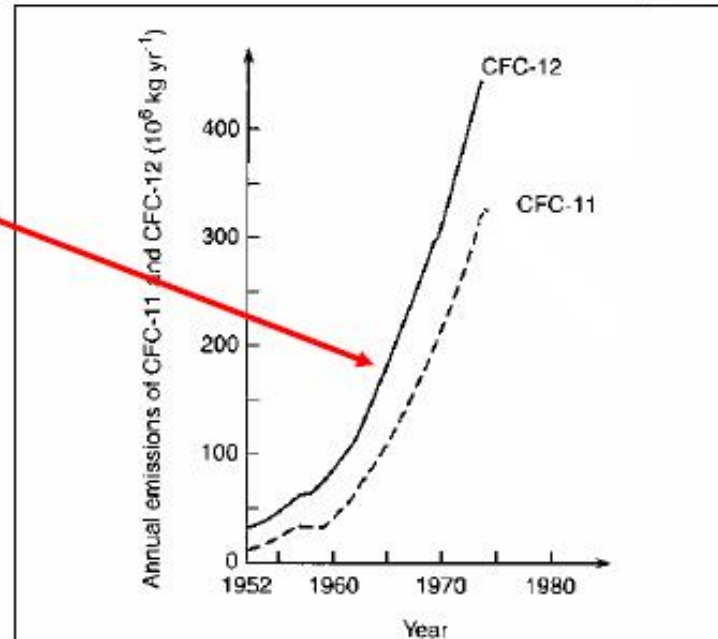
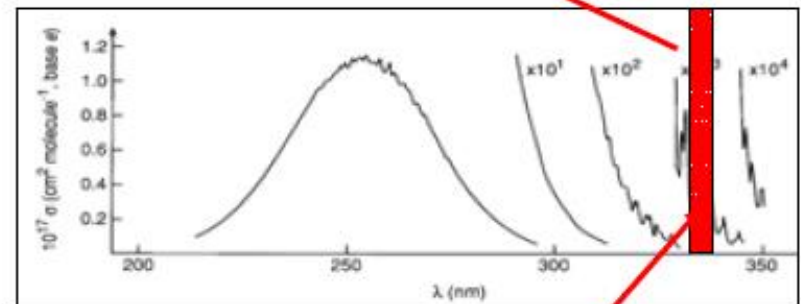
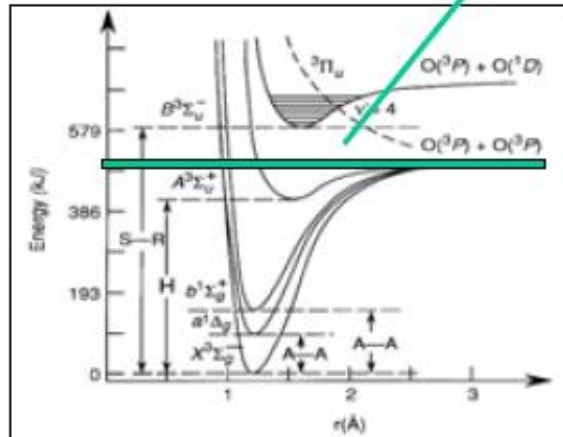
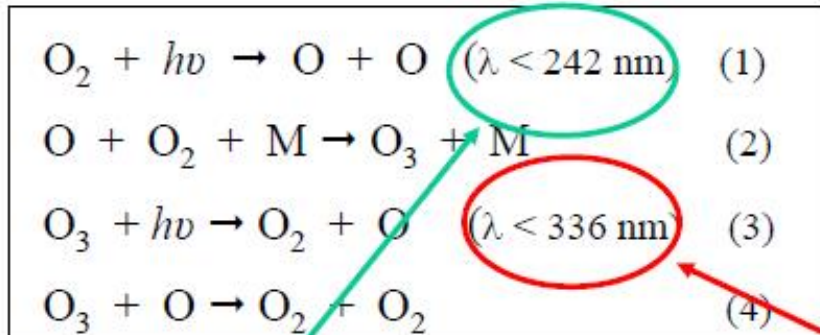


FIGURE 12.11 Estimated annual worldwide releases of CFC-11 and CFC-12 from 1952 to 1980. Data from Chemical Manufacturers' Association (adapted from National Research Council, 1984).

# Oxygen Only Chemistry (p 158-160)

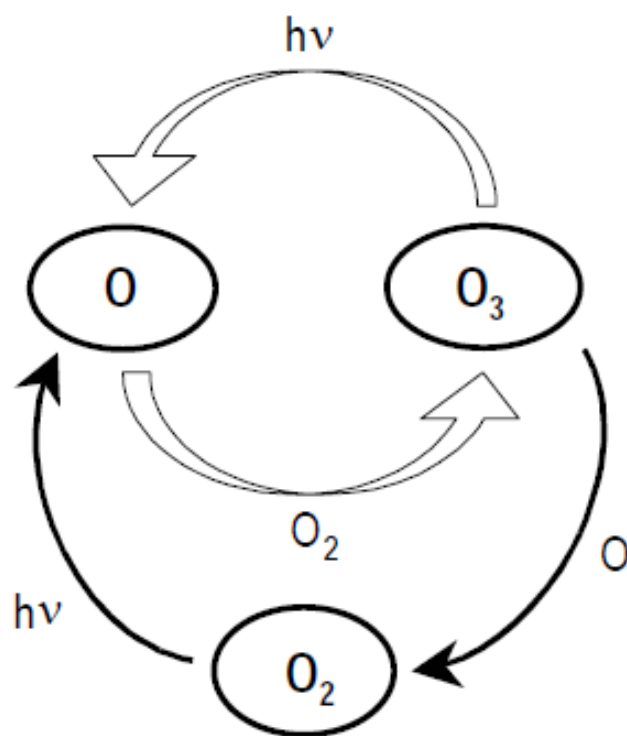


In 1930, Sydney Chapman published several theoretical papers on upper-atmospheric ozone – now known as the “Chapman Cycle”



$10^{-21}$





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

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

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

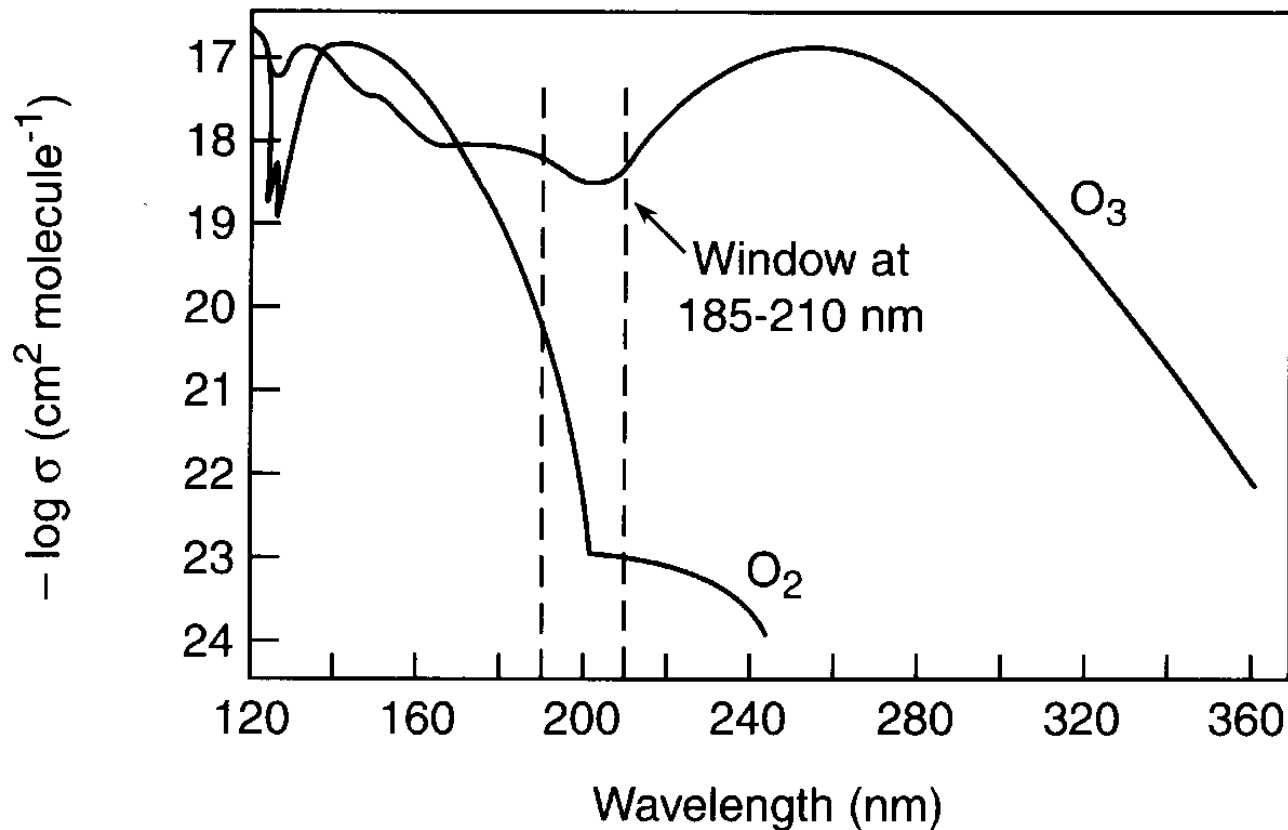
$$\text{rate 4} = k_4 [O][O_3] \quad (k_4 \approx 2 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \text{ at } 250 \text{ K})$$

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

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

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.



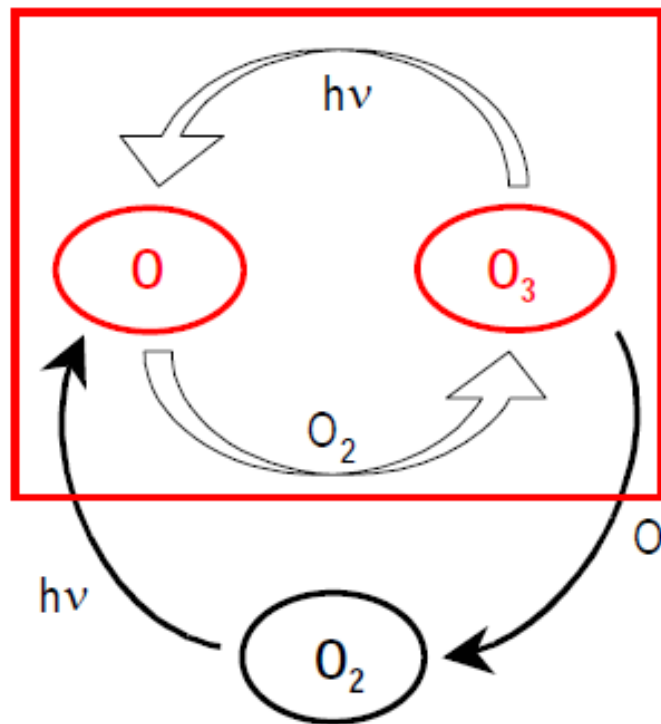
**FIGURE 12.15** Absorption cross sections for  $\text{O}_2$  and  $\text{O}_3$  from 120 to 360 nm, showing the window from  $\sim 185$  to 210 nm (adapted from Rowland and Molina, 1975).

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  $O_3$ .

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

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”



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

$$\text{Rate 2} = k_2 [O][O_2][M]$$

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

$$\text{Rate 4} = k_4 [O][O_3]$$

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

P-L

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)

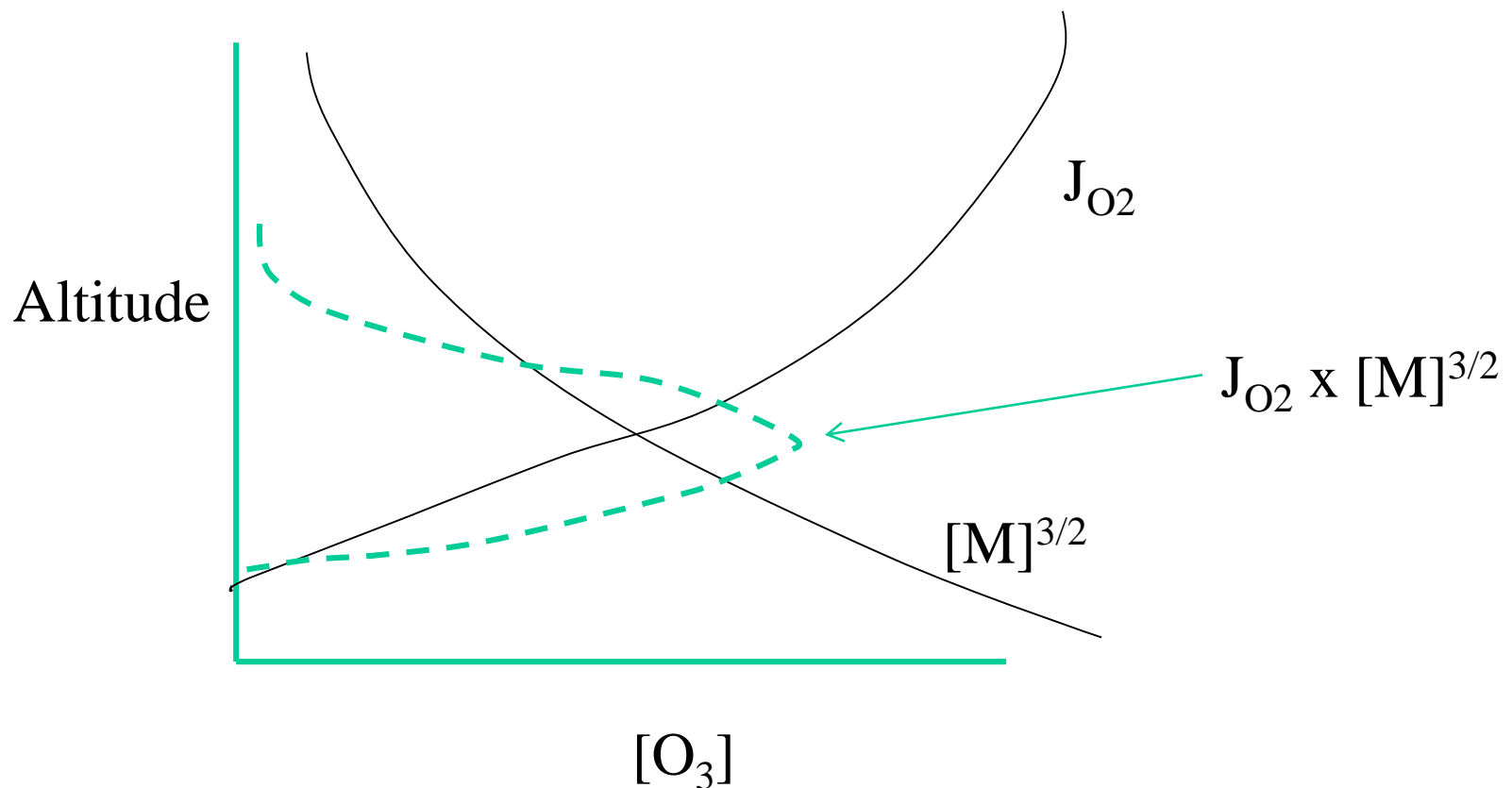
You get a similar result assuming that  $O_2$  is in steady state – the math is harder. Skip this slide if you don't care about the math!

$$\begin{aligned}\frac{d[O_2]}{dt} &= -J_1[O_2] - k_2[O][O_2][M] + J_3[O_3] + 2k_4[O][O_3] \\ &= -2J_1[O_2] + (J_1[O_2] - k_2[O][O_2][M] + J_3[O_3]) + 2k_4[O][O_3] \\ &= -2J_1[O_2] + \frac{d([O] - [O_3])}{dt} + 2k_4[O][O_3]\end{aligned}$$

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:

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

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

production

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

loss



# Chapman chemistry (in steady state)

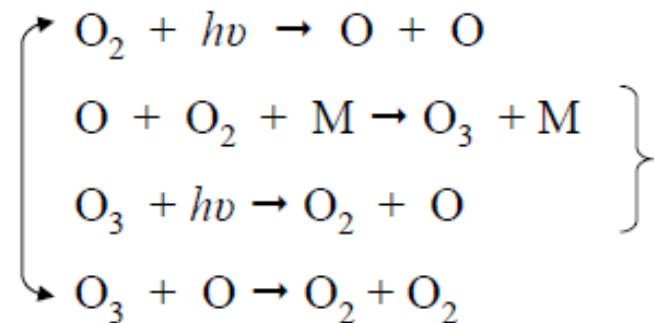
Slow and exactly  
balance



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



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



Fast and approx. balance



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



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



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

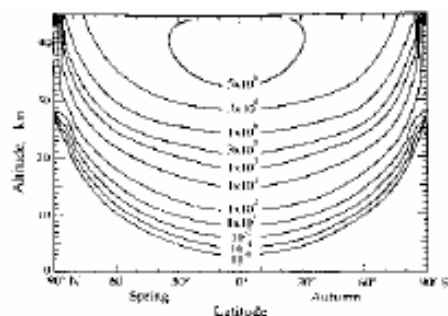


FIGURE 43. Seasonal variation of ozone concentration in molecules  $\text{cm}^{-3}$  above the poles (J. O. Anderson, 1975).

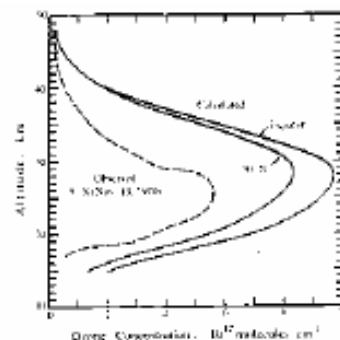
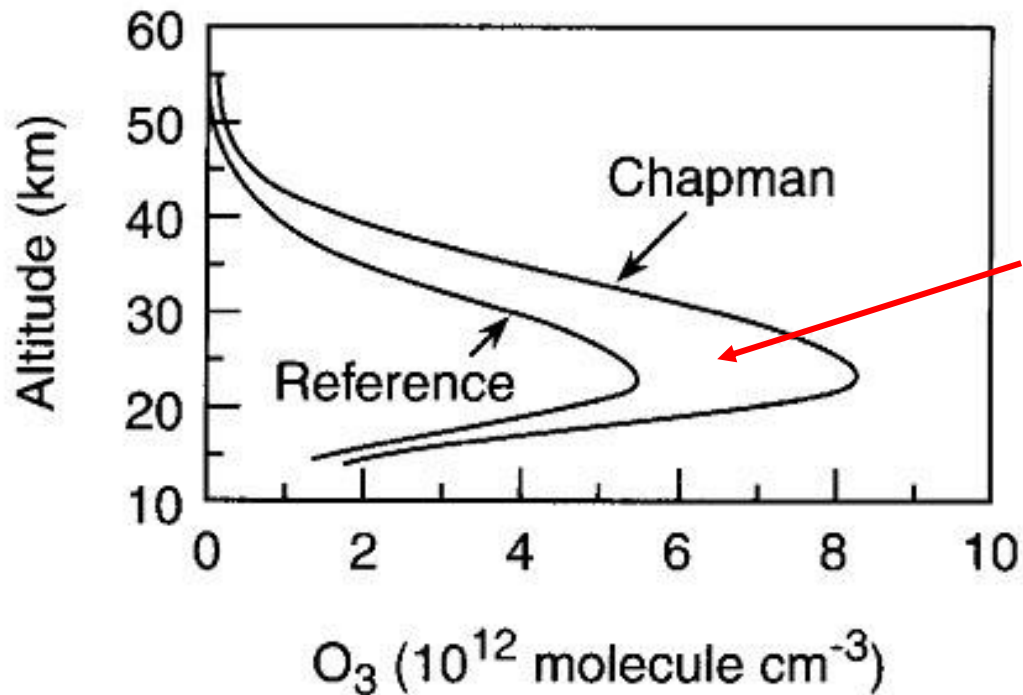


FIGURE 44. The seasonal variation of ozone concentration in molecules  $\text{cm}^{-3}$  above the poles (J. O. Anderson, 1975).

How does this compare to observations? Chapman mechanism predicts more ozone than what is observed!



What's missing?

Faster

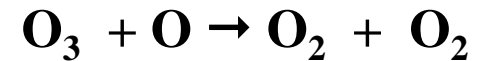
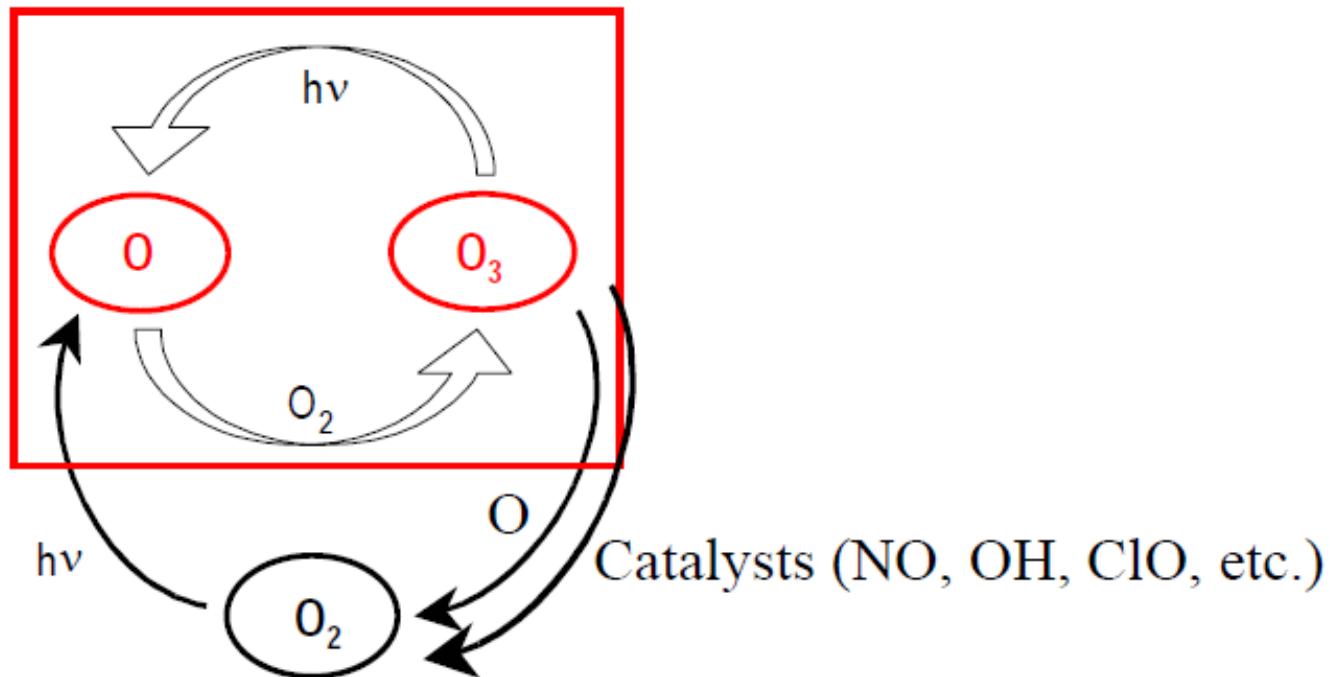
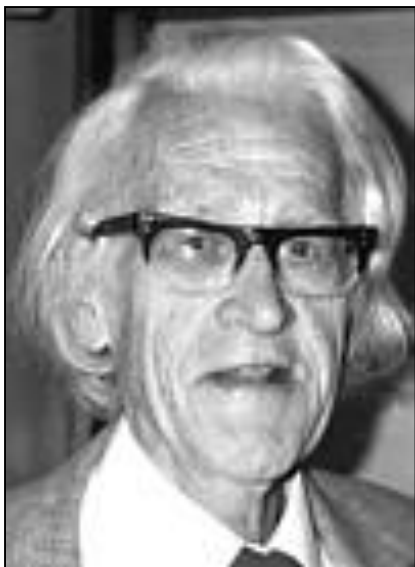


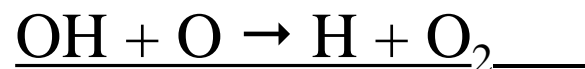
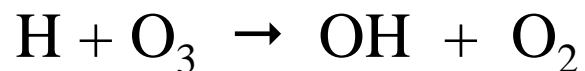
FIGURE 12.5 Model-calculated ozone vertical profiles for a Chapman or  $\text{O}_x$  model, with only  $\text{O}_2$ ,  $\text{O}$ , and  $\text{O}_3$  as reactive species and the reference atmosphere chosen to be typical of 1960 conditions (adapted from Kinnison *et al.*, 1988).

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.

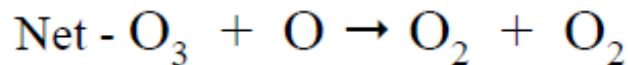
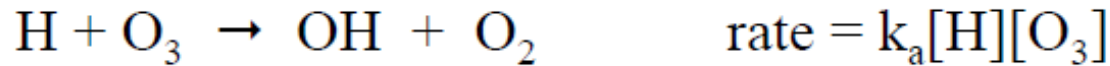




Water in the stratosphere would lead to catalytic destruction of ozone by ‘speeding up’ reaction (4) of Chapman’s mechanism – thus, introducing the concept of catalytic destruction of ozone




## Catalysis



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

Replace  $k_a[\text{H}][\text{O}_3]$  with apparent loss

$$k_a^{\text{app}} = k_a \left[ 1 + \frac{k_b[\text{OH}]}{k_a[\text{O}_3]} \right] \quad [\text{O}_3] = 0.21^2 \left( \frac{k_2}{k_a^{\text{app}}} \right)^{\frac{1}{2}} \left( \frac{J_{\text{O}_2}}{J_{\text{O}_3}} \right)^{\frac{1}{2}} [M]^{\frac{3}{2}}$$

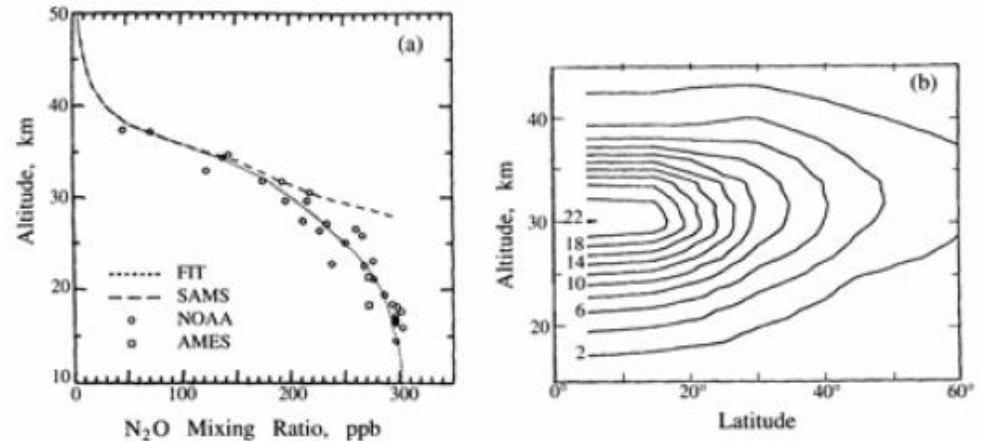
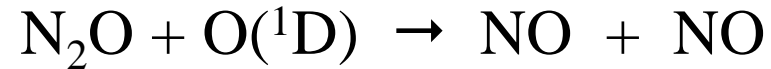

  
 >  $k_a$



## Paul J. Crutzen

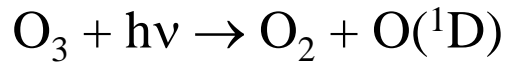
"Influence of Nitrogen Oxides on Atmospheric Ozone Content"

*Quarterly Journal of the Royal Meteorological Society* 96 (1970):320.

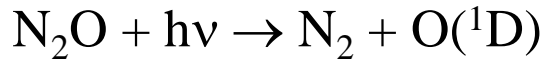


**FIGURE 4.7** (a) Vertical profiles of  $\text{N}_2\text{O}$  over the tropics at equinox circa 1980. Circles denote balloon-borne measurements at  $9^\circ \text{N}$  and  $5^\circ \text{S}$ ; squares represent aircraft measurements between  $1.6^\circ \text{S}$  and  $9.9^\circ \text{N}$ . Dashed curve refers to the average of satellite measurements at  $5^\circ \text{N}$ , 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  $\text{N}_2\text{O}$ . (b) Calculated diurnally averaged loss rate for  $\text{N}_2\text{O}$  (in units of  $10^{22} \text{ molecules cm}^{-3} \text{ s}^{-1}$ ) as a function of altitude and latitude, at equinox. The loss rate includes both photolysis and reaction with  $\text{O}(\text{}^1\text{D})$  (Minschwaner et al. 1993).

## Formation of NO<sub>x</sub>



$$J_{\text{O}_3}$$



$$J_{\text{N}_2\text{O}}$$



$$k_{2a} = 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

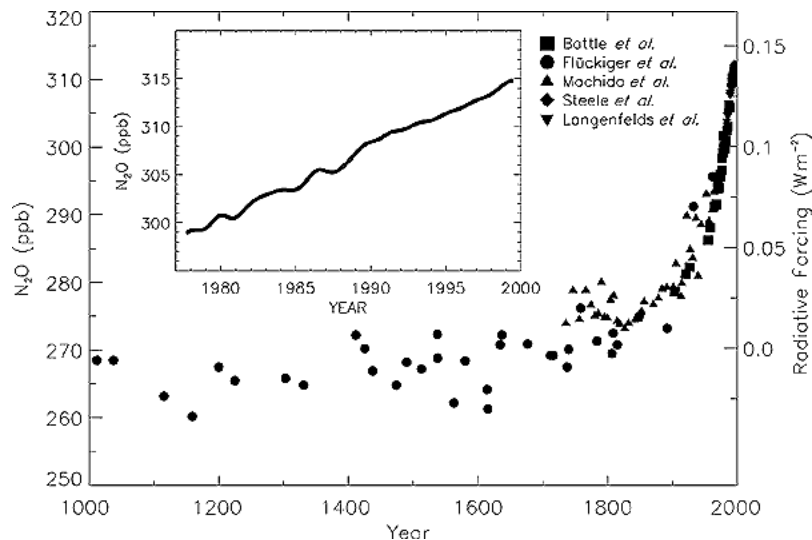


$$k_{2b} = 6.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

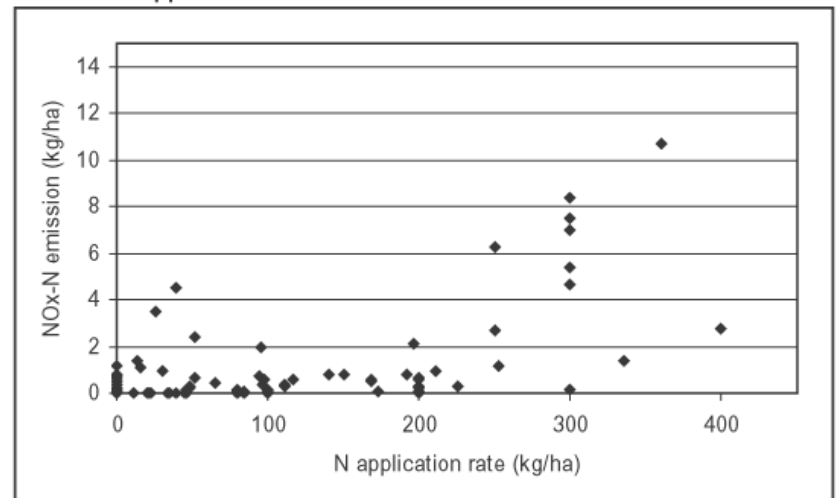
About 3-4% of the loss of N<sub>2</sub>O in the stratosphere results in the formation of nitric oxide (NO), which then acts as the main catalyst for ozone destruction. Since much of the N<sub>2</sub>O is from natural processes, this is considered a natural loss for ozone. And it is just the additional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

# Key connections made by Crutzen

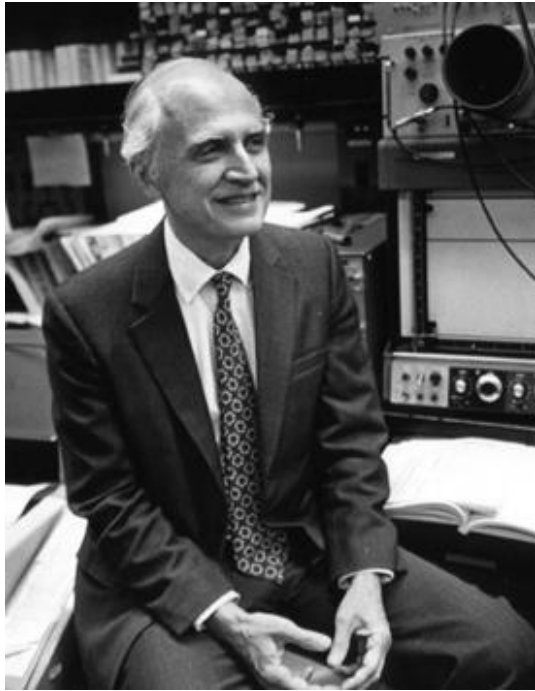
- mankind can increase  $\text{N}_2\text{O}$  emissions by fertilizing crops
- $\text{N}_2\text{O}$  has a long lifetime in troposphere, so can reach the stratosphere
- Increase in tropospheric  $\text{N}_2\text{O}$  will increase stratospheric  $\text{NO}_x$
- Increase in  $\text{NO}_x$  will result in decrease in steady state ozone
- e.g. **Mankind can alter stratospheric ozone without leaving the ground!**



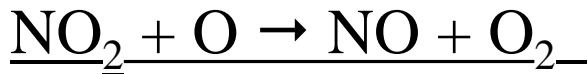
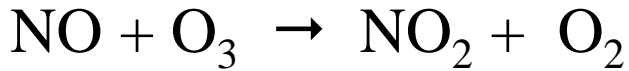
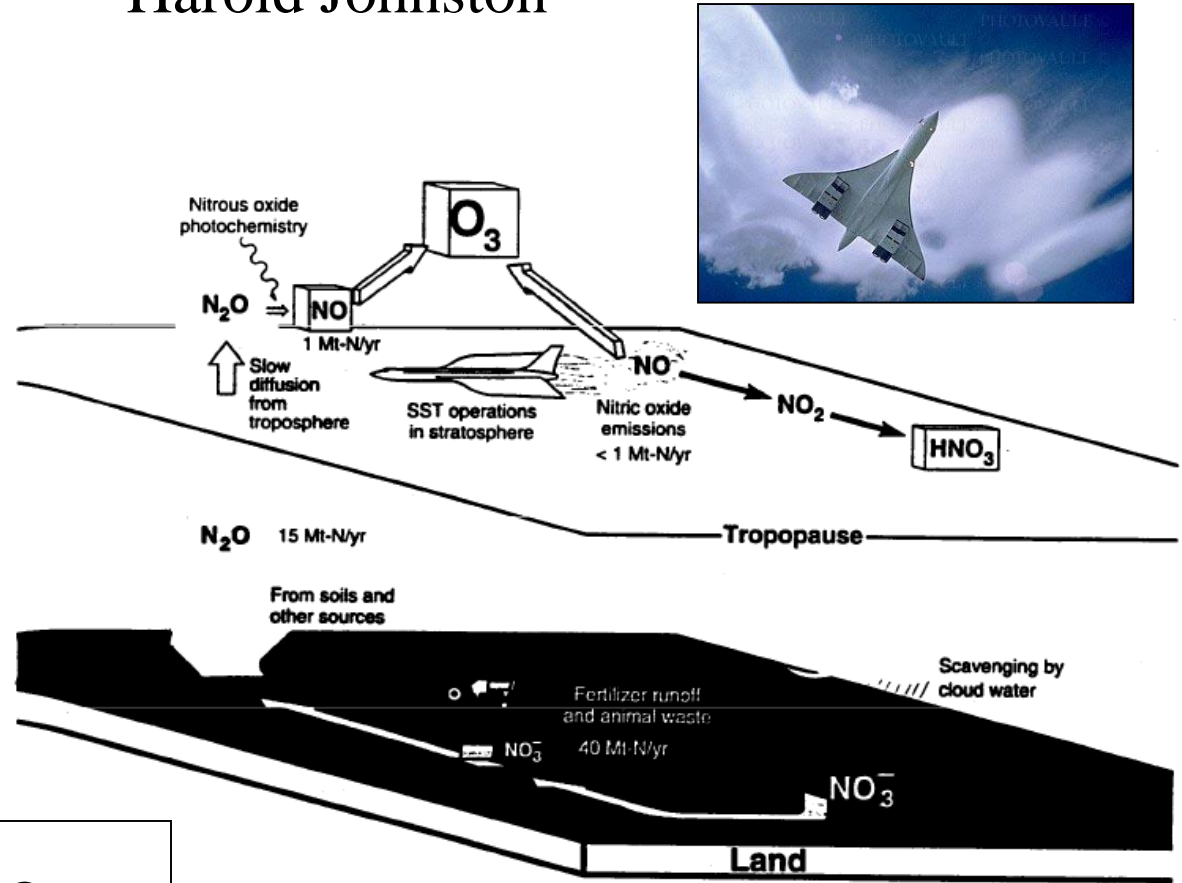
Fertilizer N application and nitrous oxide emission





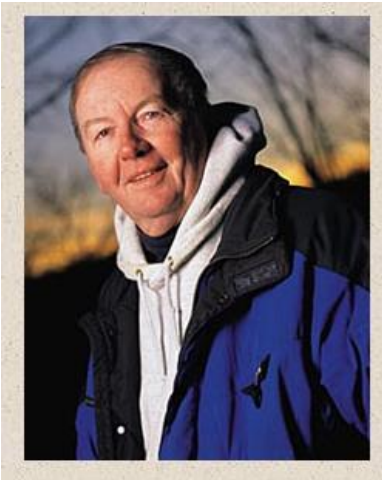


# Harold Johnston

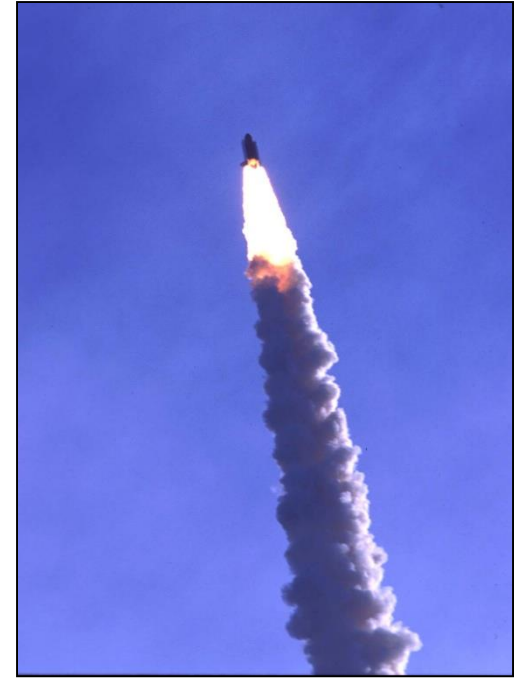
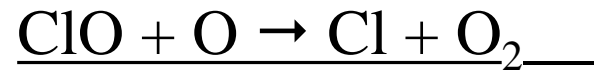
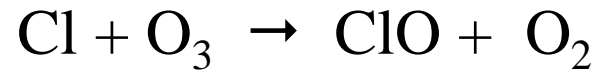


Direct Injection of emissions from SSTs

$$\frac{d[\text{O}_3]}{dt} \approx -2[\text{O}](k_{\text{O}_3}[\text{O}_3] + k_{\text{OH}}[\text{OH}] + k_{\text{NO}}[\text{NO}])$$



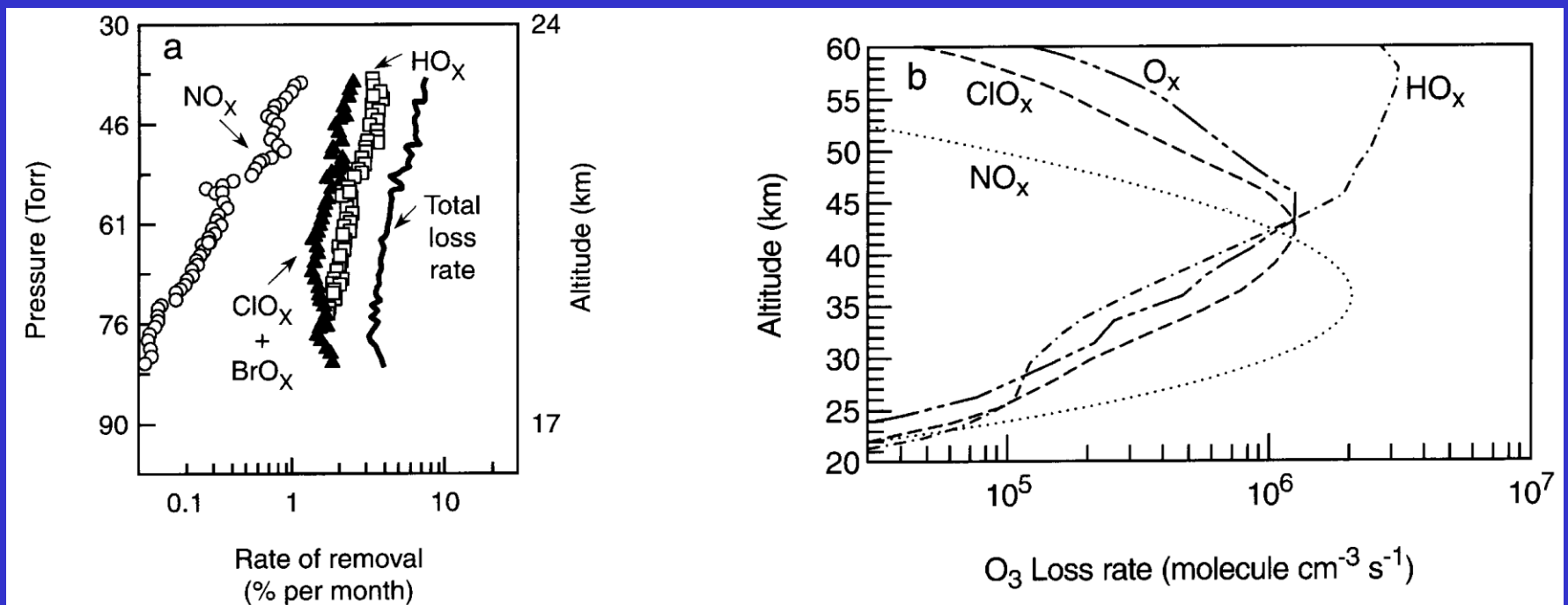
## Richard Stolarski and Ralph Cicerone



$$\frac{d[\text{O}_3]}{dt} \approx -2[\text{O}](k_{\text{O}_3}[\text{O}_3] + k_{\text{OH}}[\text{OH}] + k_{\text{NO}}[\text{NO}] + k_{\text{ClO}}[\text{ClO}])$$



We will see in a future lecture that each of these cycles contributes to ozone loss at slightly different altitudes and in different proportions.

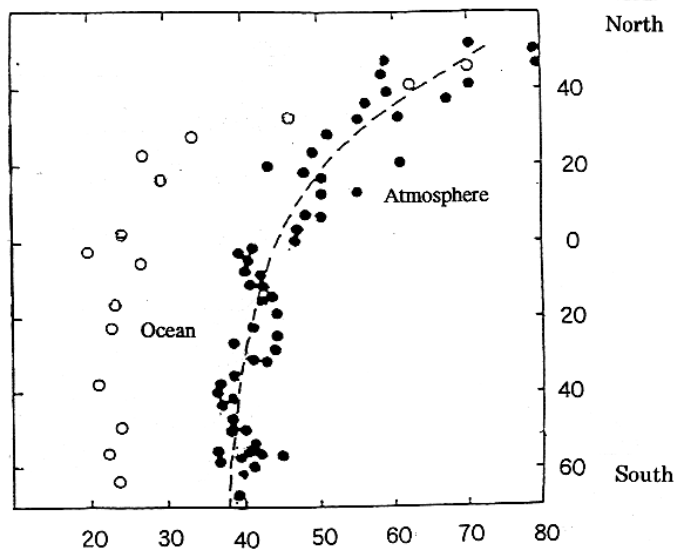
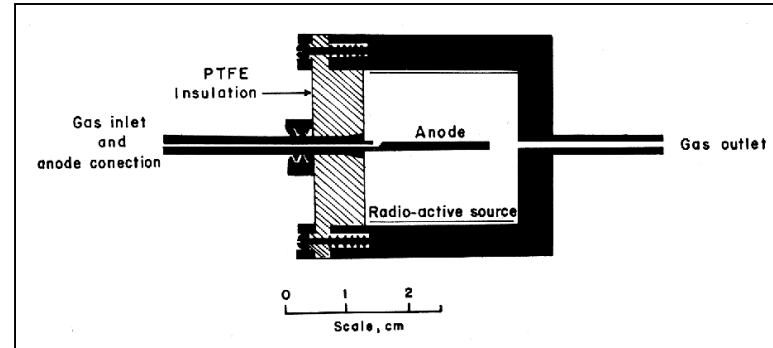


**FIGURE 12.8** (a) Rates of removal of  $O_3$  at  $38^\circ N$  in May 1993 due to  $NO_x$ , ( $ClO_x + BrO_x$ ), and  $HO_x$  chemistry, respectively, as a function of altitude in the stratosphere (adapted from Wennberg *et al.*, 1994); (b) 24-h average rates of removal of  $O_3$  as a function of altitude (adapted from Osterman *et al.*, 1997).



# Dr. James E. Lovelock, Inventor

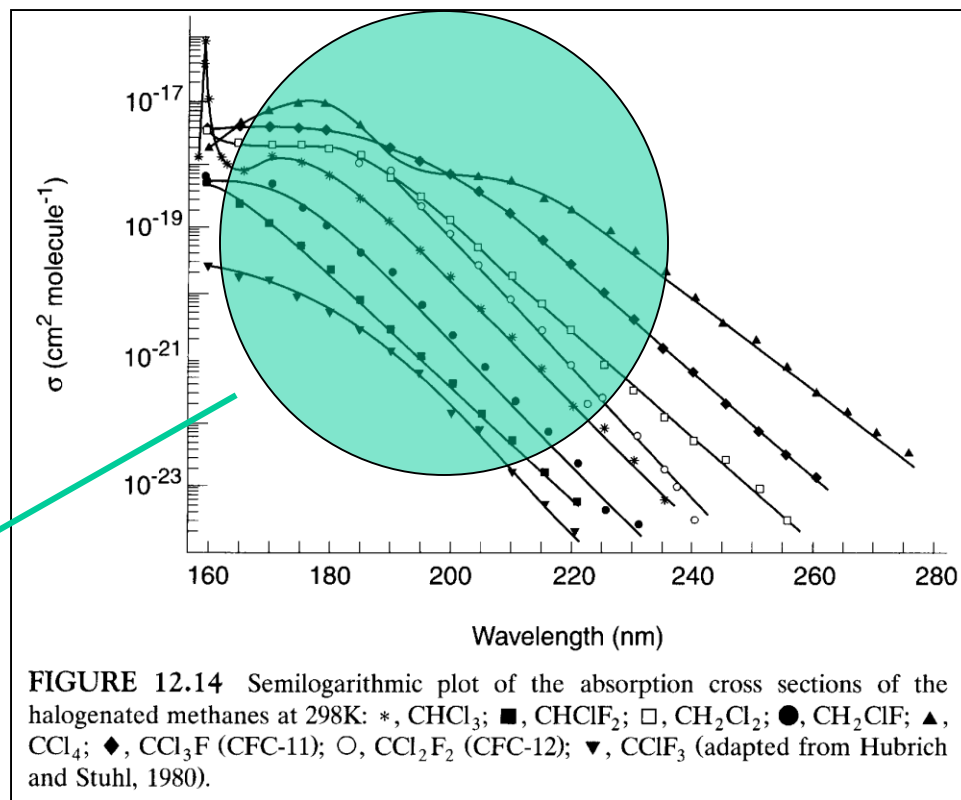
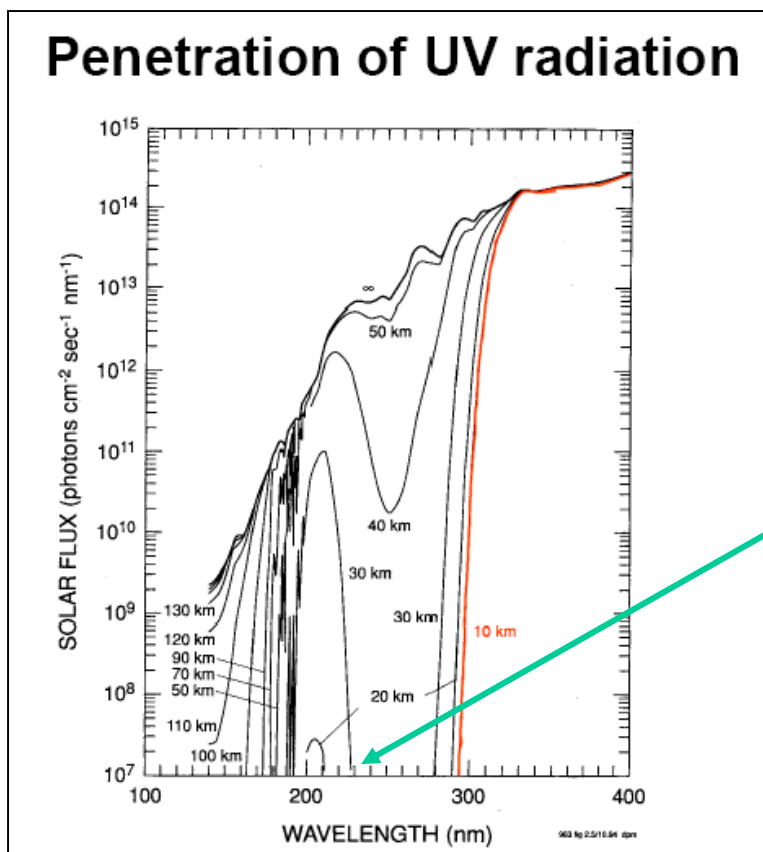
## The electron capture detector



*"...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."*

Distribution of CCl<sub>3</sub>F in and over the North and South Atlantic Ocean, Nature, Vol. 241, January 19, 1973

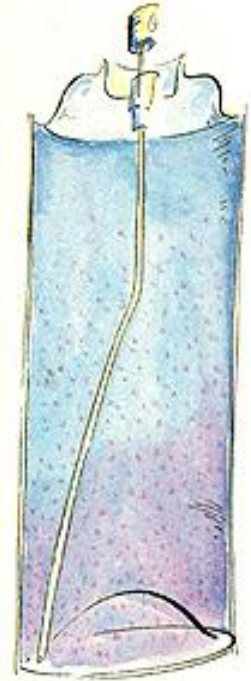
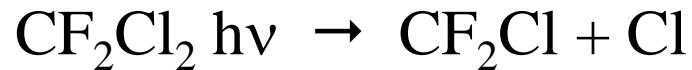
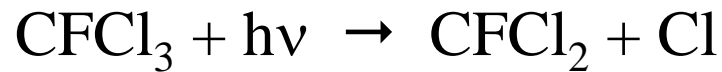
Note that chlorofluorocarbons are quite stable in the troposphere because they do not absorb sunlight. They only photolyze once they are high in the stratosphere.



# Mario Molina and F. Sherwood Rowland



Mario Molina and F. Sherwood Rowland



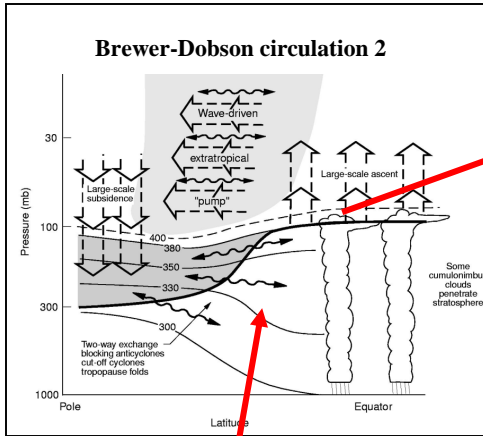
Predicted tens of percents of ozone loss

The deadly weapon!

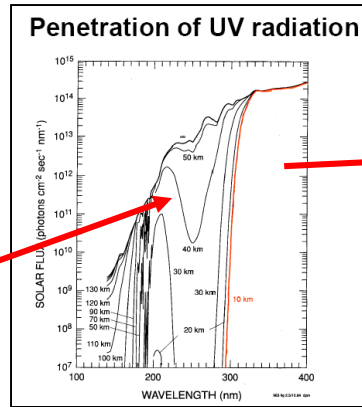
M. J. Molina and F. S. Rowland "Stratospheric Sink for Chlorofluoromethanes: Chlorine **atomic-atalsed** destruction of ozone," *Nature* 249 (28 June 1974):810

1614 citations – even with typo!

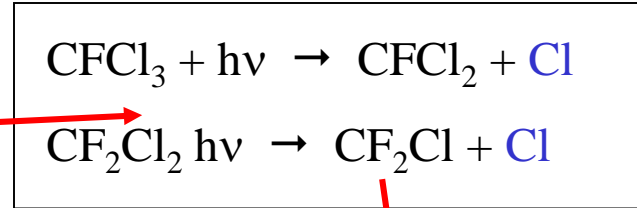
# The pieces come together!



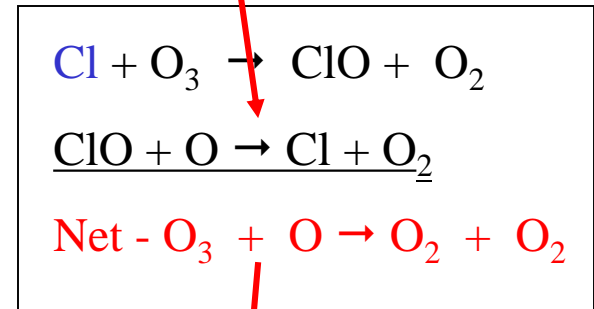
transport



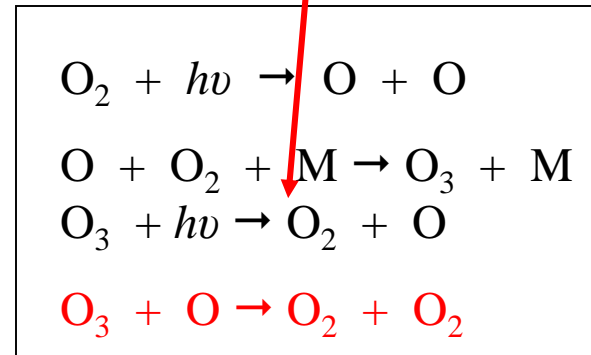
"spark"



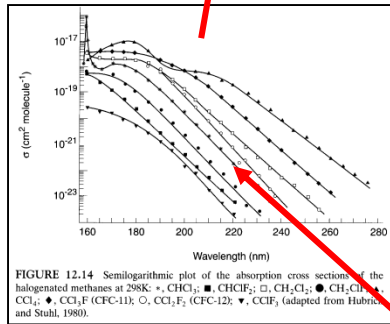
release



"flame"

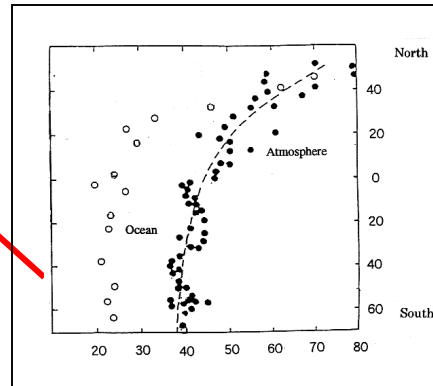


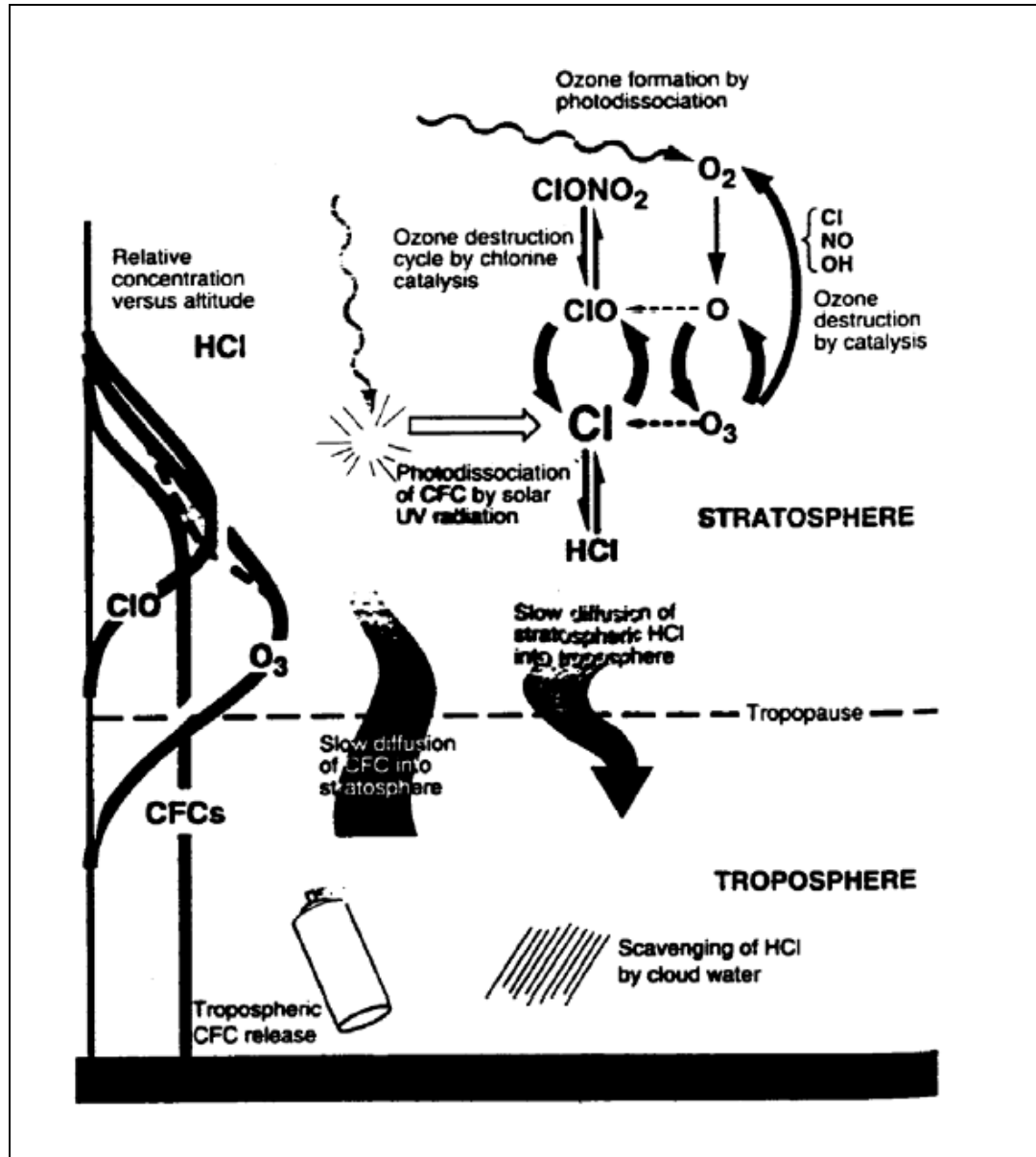
destruction



'un' reactivity

source







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

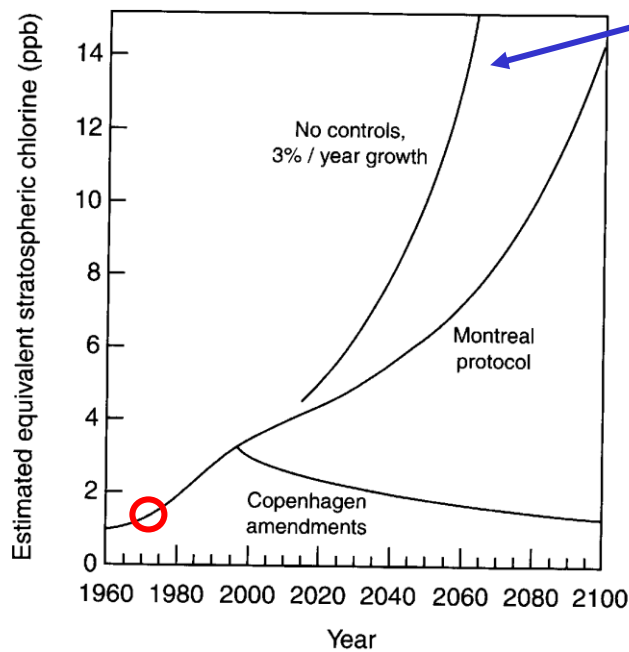


FIGURE 13.1 Estimated equivalent effective stratospheric chlorine for a continued 3% growth per year, for controls contained in the Montreal Protocol, and for those in the Copenhagen amendments (adapted from World Meteorological Organization, 1995).

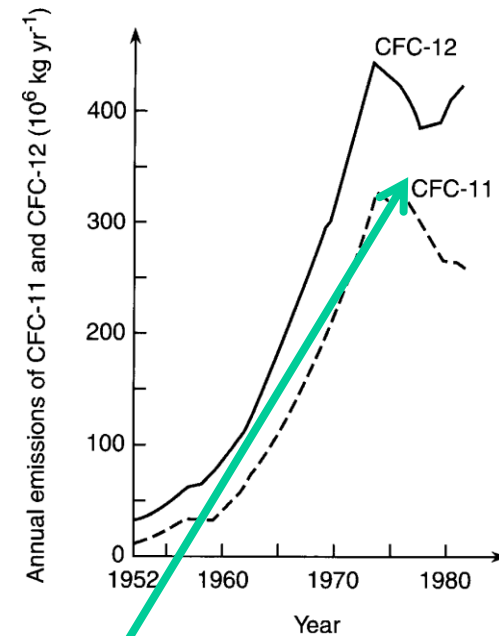
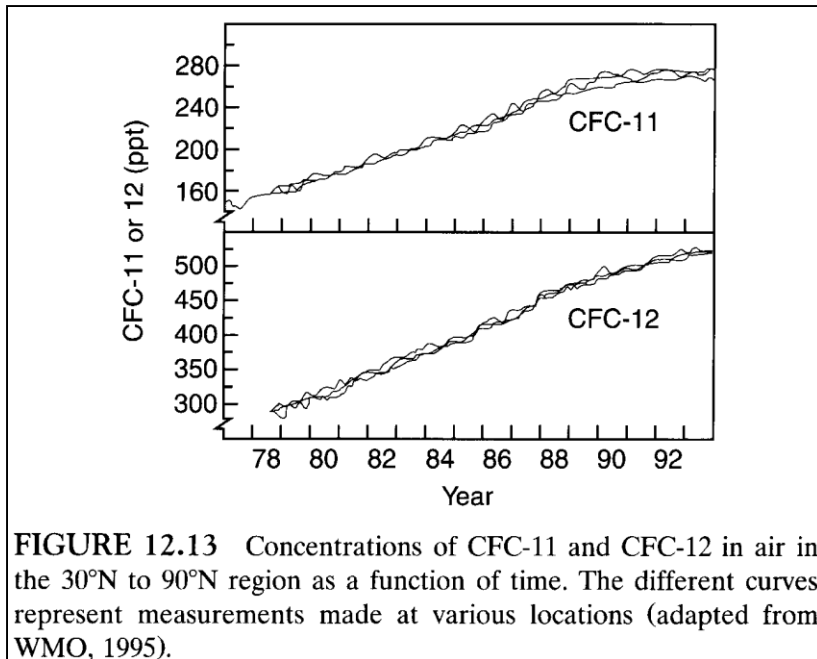


FIGURE 12.11 Estimated annual worldwide releases of CFC-11 and CFC-12 from 1952 to 1980. Data from Chemical Manufacturers' Association (adapted from National Research Council, 1984).

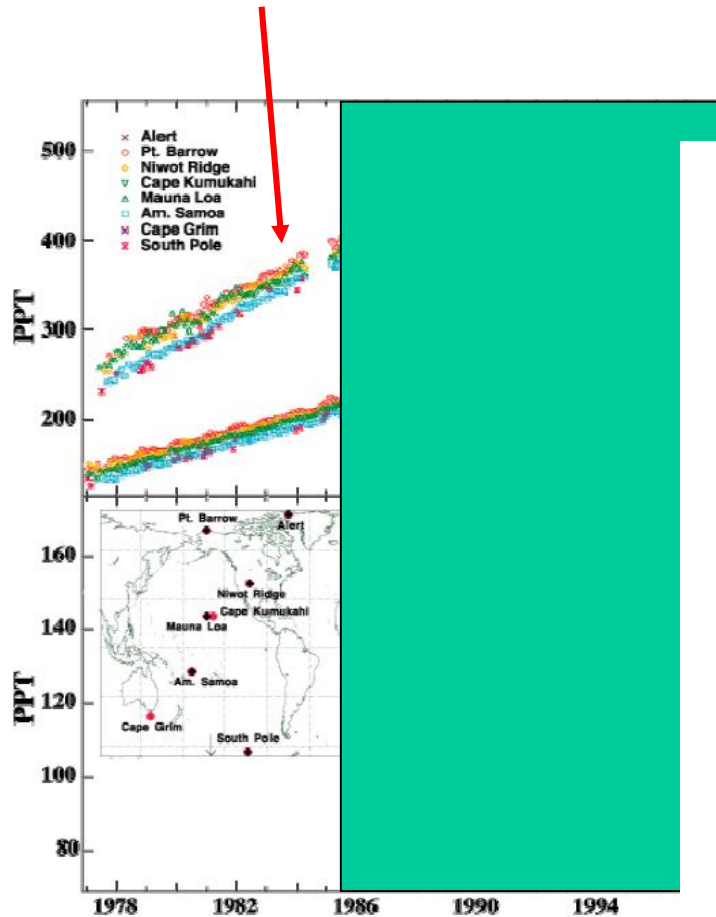
Industry pauses while it waits for word that ozone is, in fact, being depleted – i.e., let scientists look for the smoking gun!

So, all we need is  
to observe ozone losses in conjunction with  
increases in CFCs, easy, right?



→ Easy!?

CFCs nearly double over 15 years!



With no observable ozone loss!

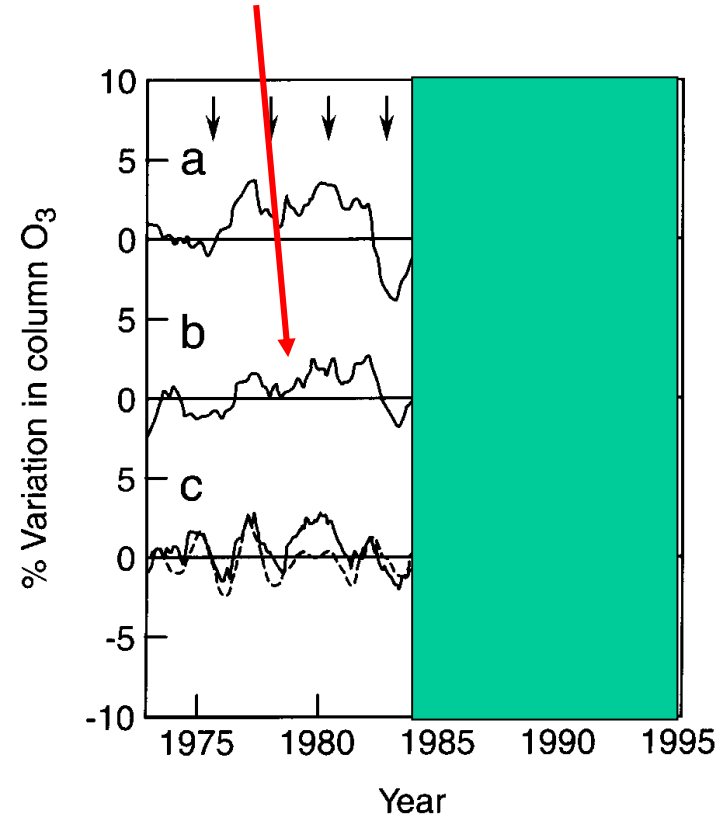


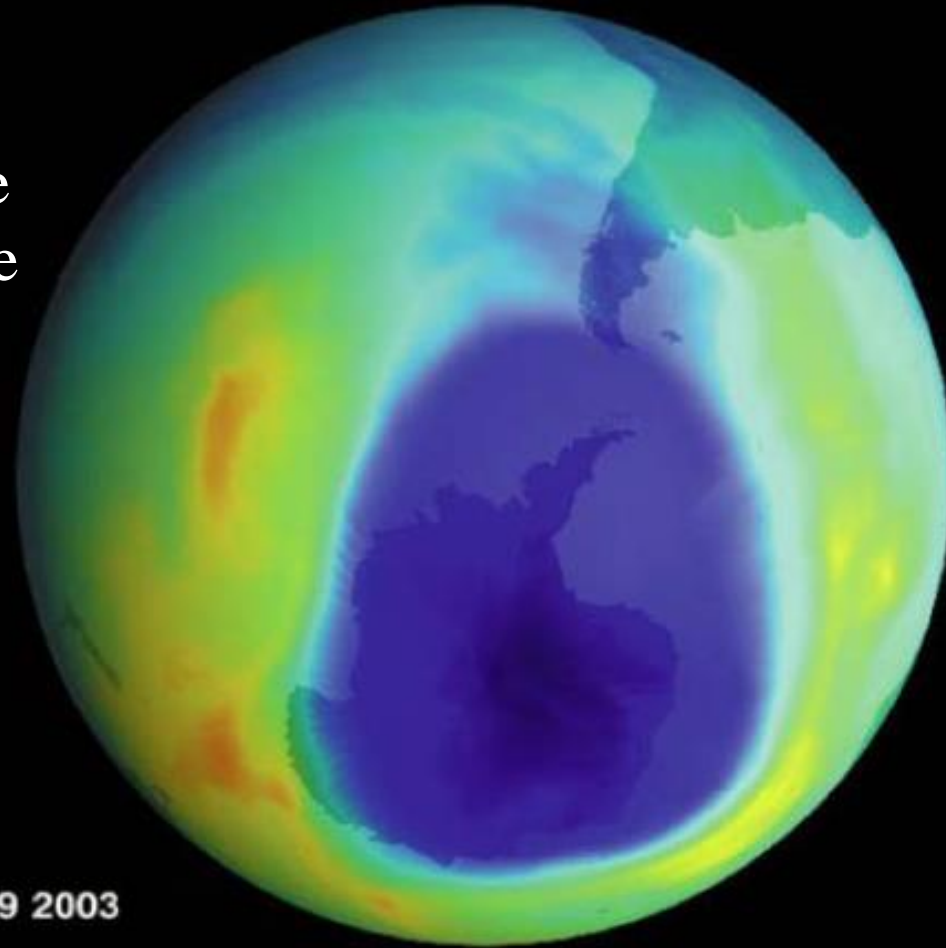
FIGURE 13.11 Percentage variations in total column ozone smoothed using a 12-month running mean for a network of stations in (a) Europe, (b) Eastern Siberia and the Far East, and (c) Western Siberia from 1973 to March 1994. The arrows show the expected QBO. In (c) the dashed line shows the component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

# The Big Surprise of 1985!

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

