2016 - Week 7 Introduction to Chemical Cycles Part 1 - Stratospheric Chemistry

Ozone – Discovery and history
The stratosphere and circulation
Chapman chemistry

Next up - explaining missing ozone loss with catalytic cycles

The Human Connection



Martinus Van Marum 1826

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!





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.









FIGURE 4.4 Zenally averaged azone concentrations (in units of 10¹⁰ molecules cm⁻¹) as a function of altitude. March 22 Gobuston, 1975). Ozone concentration at the equator peaks at an affitude of about 25 km. Over the poles the location of the maximum is between 15 and 20 km. At altitudes above the azone bulge, O₅ formation is oxygen-limited: below the bulge. O₅ formation is photonlimited.



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!





Oxygen Only Chemistry (p 158-160)

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



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 O_2 and O_3 from 120 to 360 nm, showing the window from ~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 [O₃], 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 O₃.

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

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 = $k_4[O][O_3]$

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

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 O₂ is in steady state)

Note that these reactions define a layer that has a peak somewhere above the surface. This is due to the fact that J_{O2} will be increasing with altitude (with less atmosphere above, there will be less absorption), whereas the concentration of O_2 increases with decreasing altitude.

