ATOC 3500/CHEM 3151
Week 5-6 – Additional Notes
February 16/18, 2016
On lifetimes, variability, and models

On sources and sinks

On "Stationary state," also called "steady state"

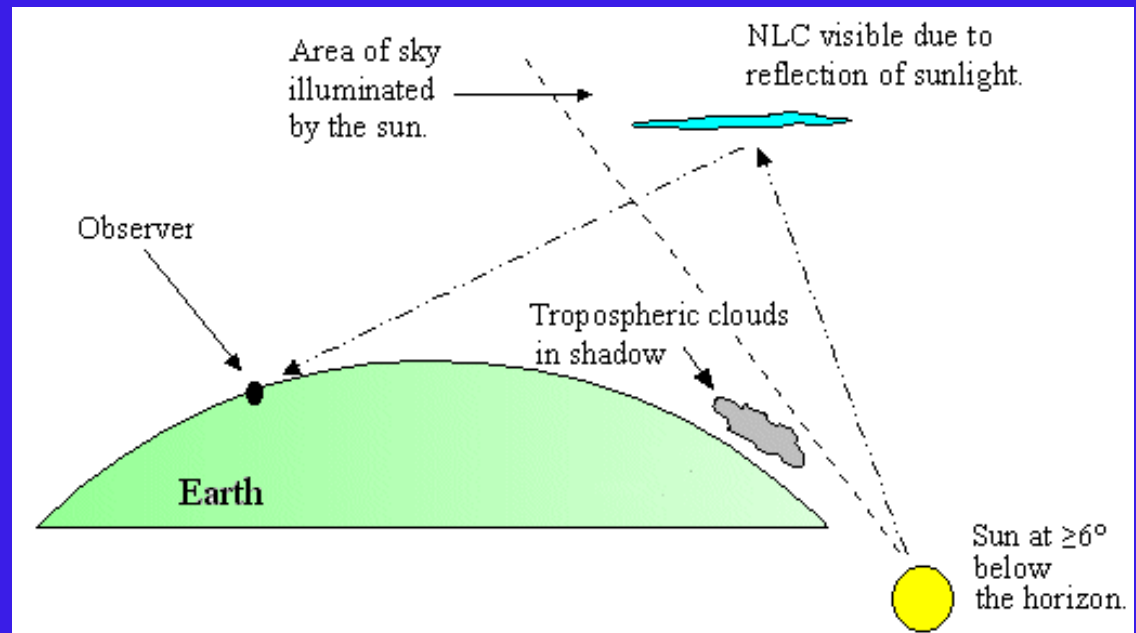Lifetimes and spatial scales of variability

On models (just about box models)

Back in 2011, a student came to class and asked about mesospheric (noctilucent) clouds, because he had been to a talk about the AIM satellite.

There are lots of pictures of noctilucent clouds on the internet.

These clouds are visible in darkness ("night luminous", or noctilucent) because they are very high – typically 80 km – which means they are still in sunlight when the Earth below is dark (because of curvature…a good factoid to tell anyone who still believes Earth is flat!). They are most certainly composed of water, although there must be some surface upon which
the water has condensed
– probably meteoritic material we also call "dust," even though it didn't originate at Earths' surface.

Area of sky illuminated by the sun.

NLC visible due to reflection of sunlight.

Observer

Tropospheric clouds in shadow

Earth

Sun at ≥6° below the horizon.

Why are these clouds interesting for this class?

Scientists have been detecting more noctilucent clouds at lower latitudes in recent decades.

This could be telling us that Earth's mesosphere is getting colder due to increases in greenhouse gases

Or, this could be telling us there is more water vapor in the upper atmosphere (source as yet unknown, but maybe rockets, small comets, or changes in transport of water from the troposphere).

Or, it could be that the increases in methane are adding water vapor to the upper atmosphere (as it must, given that methane will oxidize in the upper atmosphere). Note – each methane will produce two water molecules:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2 H_2O$$

How does methane get to the stratosphere and mesosphere?

Well, one thing for sure, it can't be super reactive in the troposphere – otherwise, it wouldn't "live" long enough to reach the stratosphere. Remember that it takes air that is released at the surface many months to travel around the globe and to mix throughout the troposphere, after which it can finally reach the stratosphere by lofting of air in the tropics
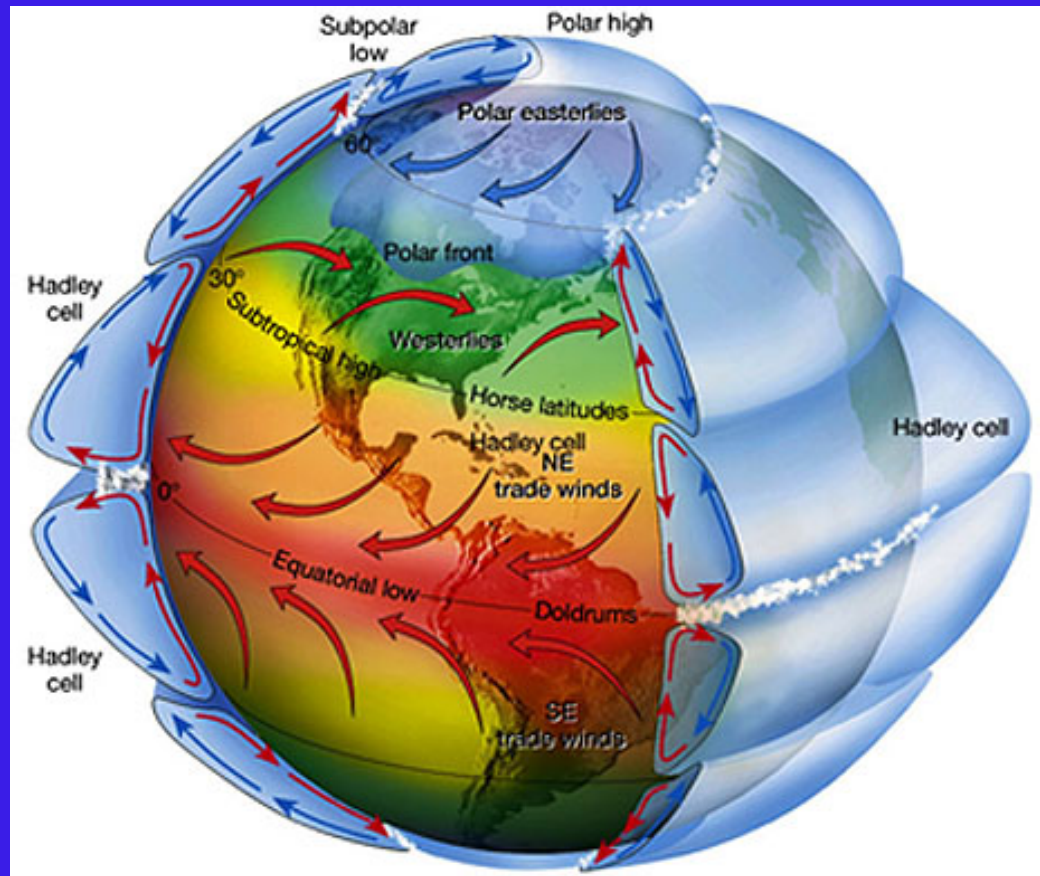
Ok, so how do we know how long it takes for methane to get to the stratosphere? We can use a very simple, but elegant proposition by Christian Junge (a German scientist who is credited with discovering the stratospheric aerosol layer in 1960) that atmospheric variability is directly related to the chemical lifetime of a compound in the atmosphere

Figure 2.1 Selected pollutants, their average residence times in the atmosphere and maximum extent of their impact
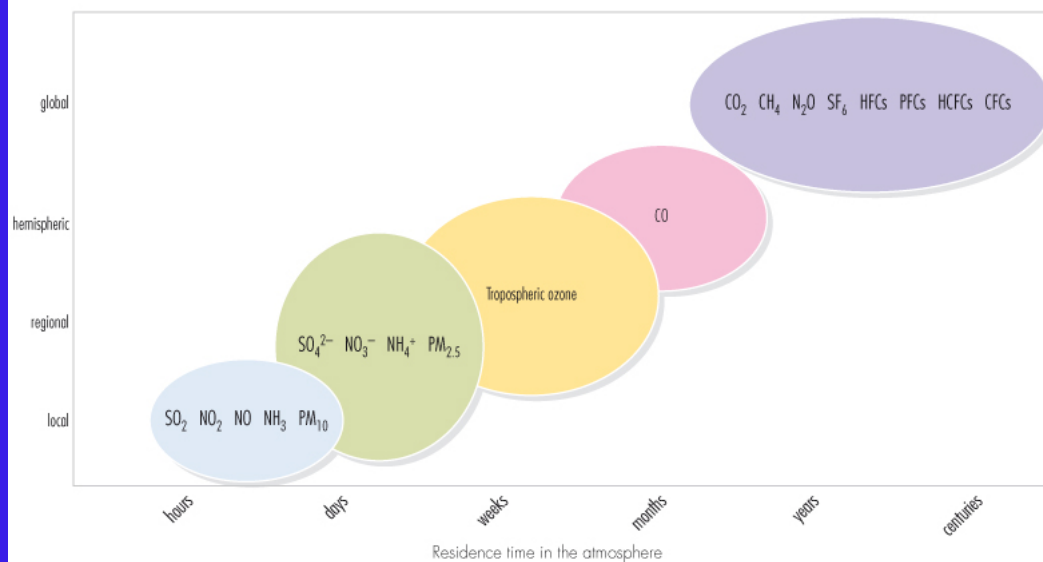
Source: EEA 1995, Centre for Airborne Organics 1997

We note that gases like CH_4, CO_2, N_2O, and SF_6, exist in the lower atmosphere at amounts that are similar around the globe. This implies that they are all pretty well mixed on timescales of years or longer, otherwise, we would find places with very high concentrations and places with low concentrations. Therefore, they must not be very reactive in the lower atmosphere

Figure 2.1 Selected pollutants, their average residence times in the atmosphere and maximum extent of their impact
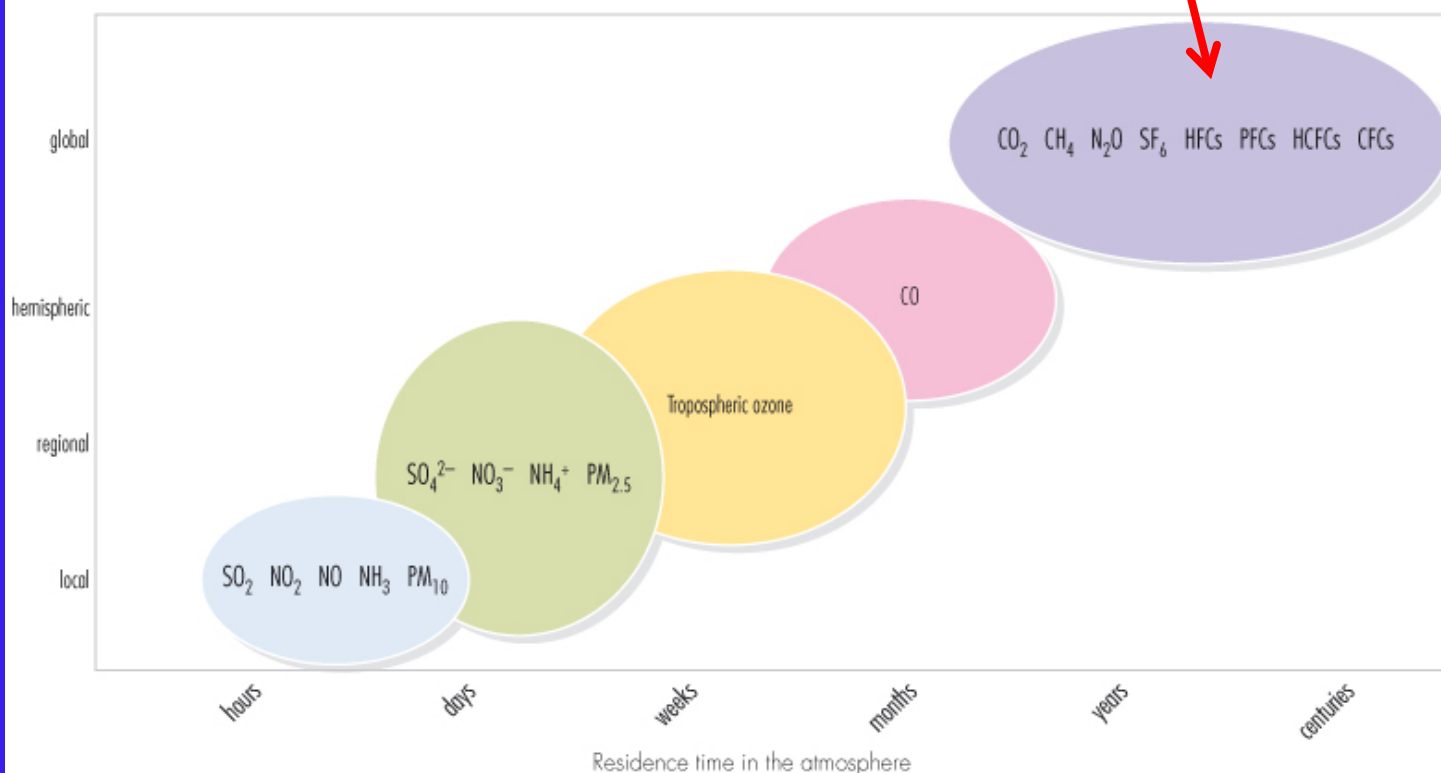
Maximum scale of the problem

global

hemispheric

regional

local

CO_2 CH_4 N_2O SF_6 HFCs PFCs HCFCs CFCs

CO

Tropospheric ozone

SO_4^{2-} NO_3^- NH_4^+ $PM_{2.5}$

SO_2 NO_2 NO NH_3 PM_{10}

hours   days   weeks   months   years   centuries
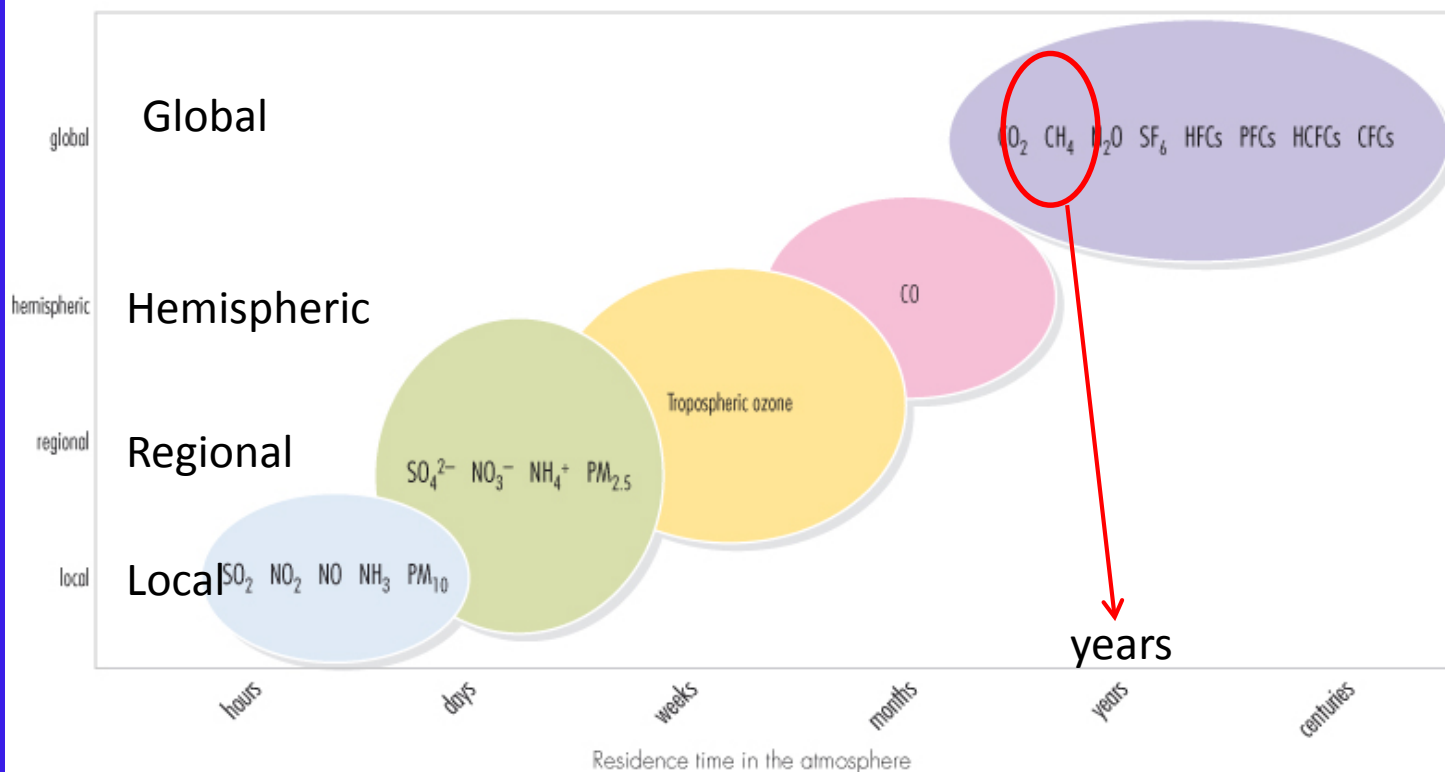
Residence time in the atmosphere

Source: EEA 1995, Centre for Airborne Organics 1997

The vertical axis is the spatial scale at which a specie is mixed (note, in the book, this is the horizontal axis). Methane has about the same concentration in the southern hemisphere as in the northern, and its primary sources are in the northern hemisphere, so this means that it has time to mix throughout the atmosphere.

Figure 2.1 Selected pollutants, their average residence times in the atmosphere and maximum extent of their impact

Maximum scale of the problem

Global

Hemispheric

Regional

Local

global
hemispheric
regional
local

CO_2 CH_4 N_2O SF_6 HFCs PFCs HCFCs CFCs

CO

Tropospheric ozone

SO_4^{2-} NO_3^- NH_4^+ $PM_{2.5}$

SO_2 NO_2 NO NH_3 PM_{10}

years

hours   days   weeks   months   years   centuries

Residence time in the atmosphere

Christian Junge

While searching for cosmic dust and debris from nuclear bomb tests, Christian Junge discovered in 1960 a layer of microscopic aerosol particles between the tropopause and about 18 miles (30 km) altitude. These particles are composed of sulfuric acid and water and are formed by the chemical transformation of sulfur-containing gases . This layer is called the *Junge Layer* or the *Stratospheric Aerosol Layer*.

Ok, so let's assume that methane is pretty well mixed in the lower atmosphere, and this means its lifetime is long. Is there another way to estimate the lifetime?

Yes! Let's take a more rigorous approach.

We'll make a simple 'box model' and use it to describe what happens to methane in the troposphere. Let's assume that there is only one source of methane (the global production rate P_{CH_4} from all processes that produce methane), and that there is only one loss process, L_{CH4}

$$P_{CH4} \rightarrow \boxed{[CH_4]} \rightarrow L_{CH4}$$

Inside our box is one number representing the concentration (or mixing ratio) of methane, and the arrow into the box represents the source (or "production") of methane to the atmosphere and the arrow out represents the sink (or "loss") of methane from the atmosphere.
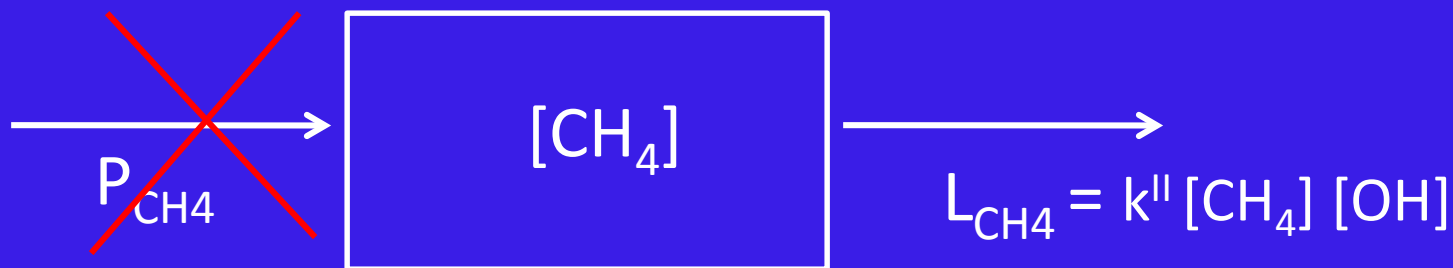
$$P_{CH4} \longrightarrow \boxed{[CH_4]} \longrightarrow L_{CH4}$$

We just add up all the known sources of methane to get P, and we note that the main loss of methane is the reaction with OH (see page 65):

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$\text{Rate} = -\,d[CH_4]/dt = k^{II}\,[CH_4]\,[OH]$$

Our box model is pretty simple, but it is really how we deal with much more complicated problems – we just add more boxes that represent different parts of the atmosphere to look at horizontal and vertical variations, and we add more sources and sinks (more 'arrows') if we know that there is more than one way to produce or destroy our compound of interest.

More on that later – but for now, let's look at some important results that we can deduce from our simple box model. Let's examine what happens if we use the rate of the reaction from the previous page and assume that there is no source of methane.

$$[CH_4]$$

$$P_{CH4}$$

$$L_{CH4} = k^{II} [CH_4] [OH]$$

We can write the rate of change of methane as:

$$d[CH_4]/dt = P_{CH4} - L_{CH4}$$

$$= 0 - k^{II}[CH_4][OH]$$

Or, dividing by $[CH_4]$ and multiplying by dt,

$$d[CH_4]/[CH_4] = -k^{II}[OH] dt$$

This is easy to solve:

$$[CH_4]/[CH_4]_o = exp\{-k^{II}[OH]t\}$$

This is an exponential loss of CH_4 with a characteristic time constant of $(k^{II}[OH])^{-1}$. Note that the time it takes for methane to decrease to $1/e$ of its original value does not depend on how much CH_4 we start with.

We can get the same result by noting the following:

"Lifetime of CH_4" $= \tau_{CH4} = [CH_4] / k^{II} [CH_4] [OH]$

$$\tau_{CH4} = 1 / (k^{II} [OH])$$

We note that "lifetime of methane" means the time that it takes for the concentration to drop to 1/e of the original value.

Note the units. k^{II} is cm^3 molecule^{-1} s^{-1}, so:

$\tau_{CH4} = 1 / (cm^3$ molecule^{-1} s^{-1} molecule cm^3]$) = 1 / s^{-1} = s$

Some terminology we get from this 'box model.'

"Reservoir" refers to the amount of X we have in the box – just like a 'reservoir of water' refers to the quantity of water.

Production (or source) – rate at which X is added to the box

Loss (or sink) – rate at which X is removed from the box

Lifetime – how long it takes for [X] to decrease to 1/e [X]. Also, a characteristic timescale that we can then compare to spatial variations in the "Junge variability lifetime" plot we looked at earlier.

On February 11, I described where OH comes from in the atmosphere. (Don't do like I did when I was examined on this in order to continue with my PhD work – I should have known the answer, but at that time, I didn't!)

I have seen written in a number of places that the main source of OH in the atmosphere is photolysis (absorption of sunlight which breaks a molecular bond). In fact, H_2O is very stable, and doesn't absorb UV light except high up in the upper stratosphere and mesosphere. But there is a photolysis step that is essential to produce OH.

When ozone (O_3) absorbs ultraviolet light, a very small amount of a special type of oxygen atom, called "O singlet D," or $O(^1D)$, is produced. This $O(^1D)$ atom is very unstable, and whenever it collides with another molecule it either reacts with that molecule or it's electronic state is changed and it becomes more stable.

We will discuss where O(^{1}D) comes from a little later when we look at ozone chemistry. Let's look at what O(1D) does typically in the atmosphere. The most likely collision is with N_2 or O_2, the most abundant species in the atmosphere.

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2$$
$$O(^1D) + O_2 \rightarrow O(^3P) + O_2$$
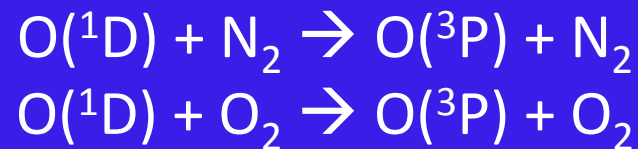
Note, these two reactions don't do much, other than to change the state of the oxygen atom (and put some energy into the N_2 and O_2 molecules that eventually ends up as heat in the atmosphere). But when it reacts with H2O, it breaks the molecule in half.
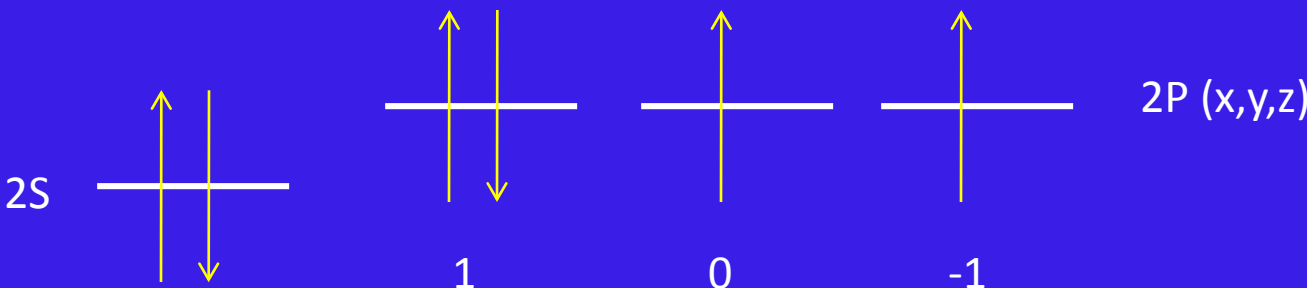
$$O(^1D) + H_2O \rightarrow OH + OH$$

O(^{1}D) and O(^{3}P) get their names (actually called "term symbols") from the arrangement of electrons. In a normal (ground state) oxygen atom, the valence electrons are situated in 2S and 2P orbitals in the following way:

2S   1   0   -1   2P (x,y,z)
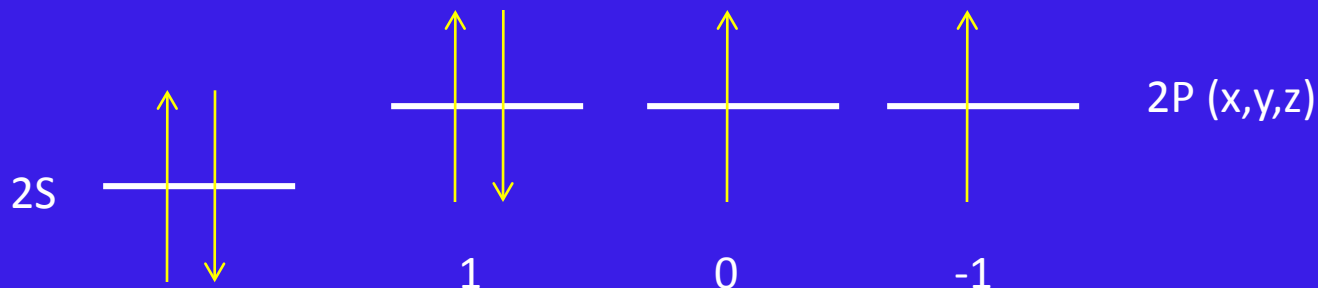
We write this as: $(2S)^2 (2P_x)^2 (2P_y)^1 (2P_z)^1$

Note that there are two electrons with unpaired spins (so O is a bi-radical)

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2S

2P (x,y,z)

1   0   -1

The lettered symbol "S, P, or D" is based on the shape of the orbital, which in some sense is like angular momentum. Each electron in the 2S orbital is given a value of 0, and each in P_x is given a value of 1, each in P_y is given 0, and each in P_z is given -1. So in the configuration above, the total angular momentum is (0 + 0 + 1 + 1 +0 - 1) = 1. We call this a "P" state.

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2P (x,y,z)

2S

1   0   -1
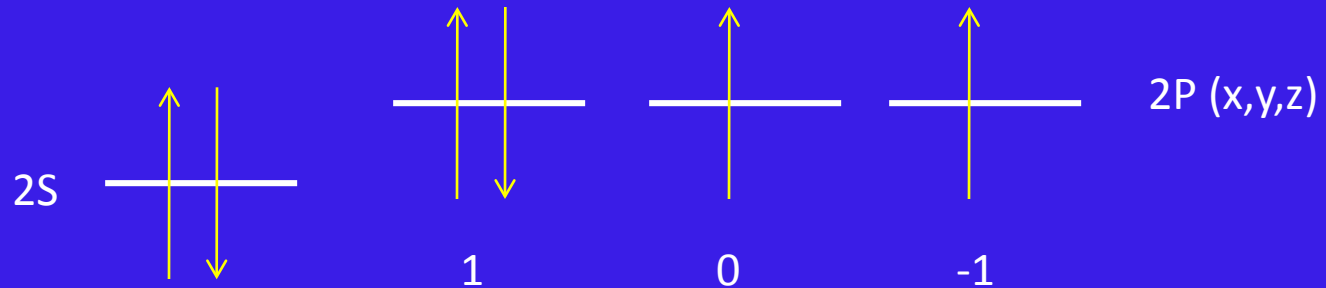
Each spin is given a value of ½ or -½, so the total spin above is +1, which is called a 'triplet' because this state will give three peaks in a spectrum taken in a magnetic field (something called "Zeeman splitting."

So this configuration is called ^{3}P, or "triplet P."

In O(^{1}D), one of the electrons has its spin reversed and paired up with the other electron that was unpaired in the ground state O(^{3}P). This might look more stable, but in fact, an empty orbital is far more reactive than a half-filled one, so this configuration is ultra-reactive.

2S

2P (x,y,z)

1   0   -1
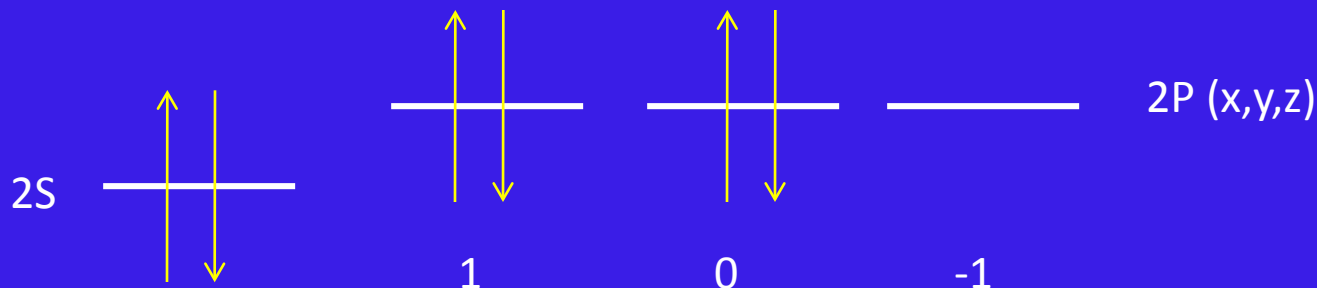
We write this as: $(2S)^2 (2P_x)^2 (2P_y)^2 (2P_z)^0$

Total angular momentum for this arrangement is 2, which we call "D," and the spin is 0, which is 'singlet' or superscript 1, hence, O(^{1}D).

Note – what makes O(^{1}D) so reactive is that if another molecule collides with it, the open orbital can simply attach to the other molecule, forming a new bond, but in the process, a huge amount of energy is released, and this if often fatal to that new molecule, which falls apart rapidly.