ATOC 3500/CHEM 3151
Air Pollution Chemistry
Lecture 1

Note – Page numbers refer to Daniel Jacob's online textbook: http://acmg.seas.harvard.edu/publications/jacobbook/index.html

"Atmos" = vapor + "sphaira" = ball

What is Air? (DJ Pages 1-2)

Nitrogen (N_2), comprising 78.08% of air
Oxygen (O_2), comprising 20.95% of air
Argon (Ar), comprising 0.93% of air.

The sum of these 3 is 99.96% (if we first remove the water – we call this "dry mixing ratio")

All of the other noble gases (He, Ne, Kr, Xe) are present in the atmosphere, but at very small quantities. These and the three major gases are "well-mixed"; that is, their fractions do not vary in the lowest 100 km of the atmosphere (called the "homosphere").

For more on the noble gases, and other species, see http://www.gly.uga.edu/railsback/Fundamentals/AtmosphereCompIII.pdf

Chapter 1 – Basics of the Atmosphere

Gases and suspensions of particles in gases ('aerosols') are both important to the chemistry of Earth's atmosphere

All gases have some role to play, but amazingly, even those that are present in very small trace amounts can have important roles. In a number of cases (like the Antarctic Ozone Hole), a molecule that is present in ten parts out of 1 trillion total molecules ('10 parts per trillion') is more important than gases that are present at thousands of times larger amounts.

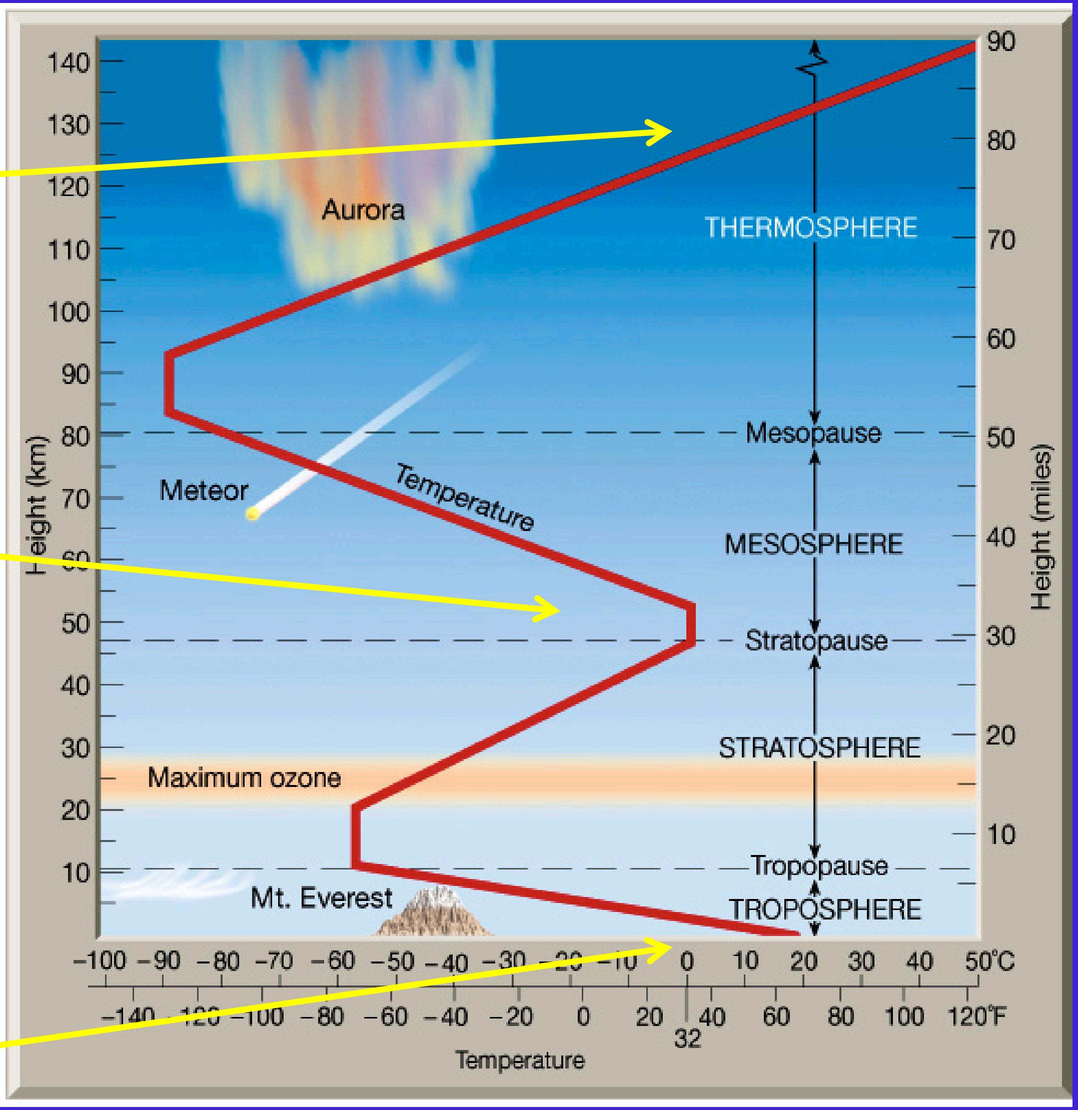
This is what atmospheric chemistry so challenging – it's also what makes it very exciting, as we'll see during the semester.

Vertical structure of the atmosphere
Established by chemistry (DJ Pages 14-15)

The thermosphere is warm due to absorption of high energy light (Xray, Gamma Ray, shortwave ultraviolet or UV) by lots of things

The stratosphere is warm due to absorption of longwave UV light by ozone (O_3)

The surface is warmed by absorption of visible light from the sun and thermal (infrared) radiation trapped by greenhouse gases



Particles and clouds also impact atmospheric composition (DJ Pages 178-186)

This is a picture of polar stratospheric clouds from Kiruna, Sweden, taken from a parking lot at the airport where I was studying ozone depletion in winter of 1999-2000. The sun has set – these clouds are 22 km above the surface, well in the stratosphere, so they are still lit by the sun. These clouds are made of ice, and they are responsible for altering the normal chlorine chemistry in the ozone layer, thereby leading to ozone holes that are seen over Antarctica and the Arctic.

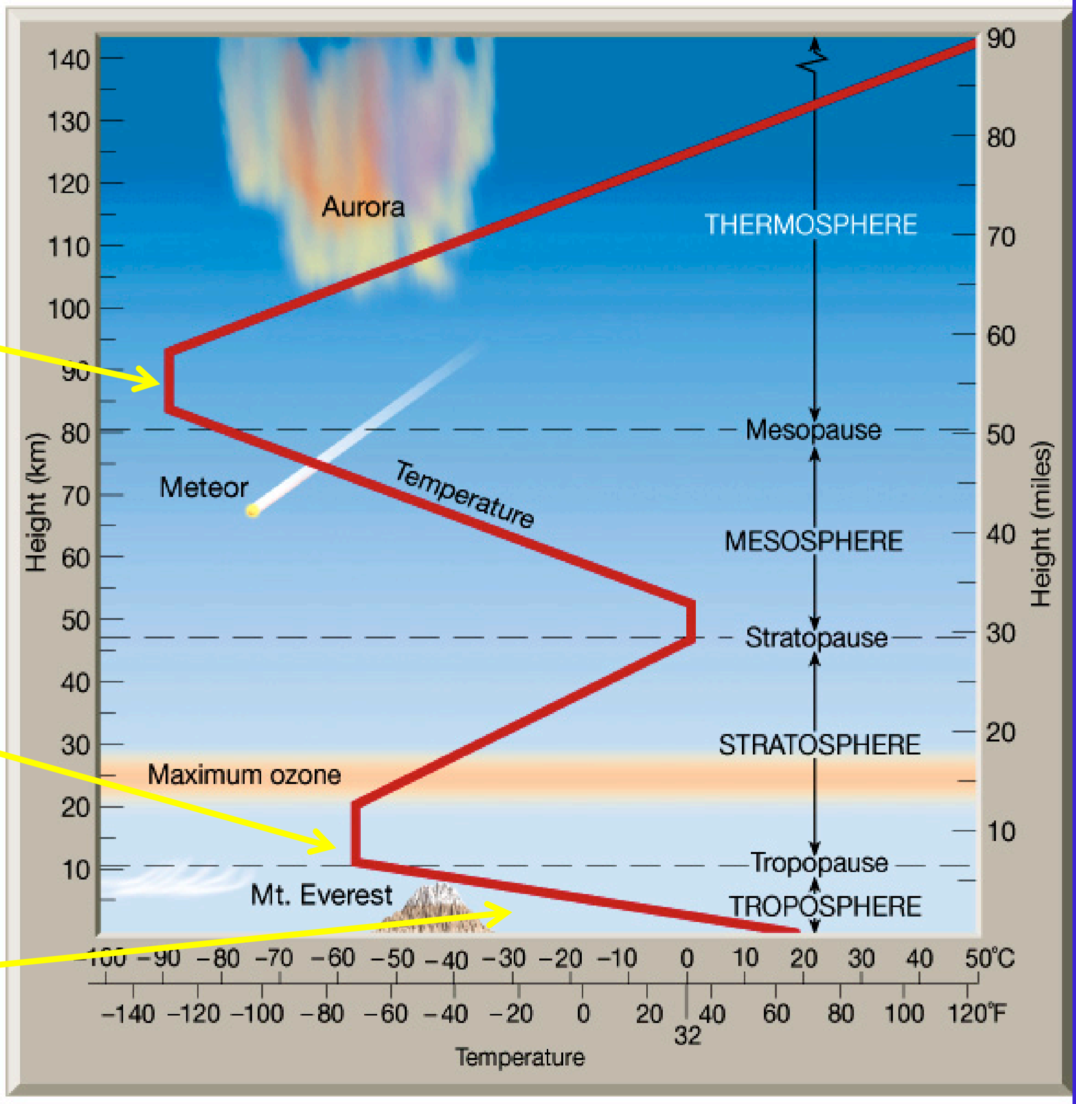
Where do clouds form?

In cold regions at high altitudes:

Noctilucent clouds (can see at night because they are high altitude)

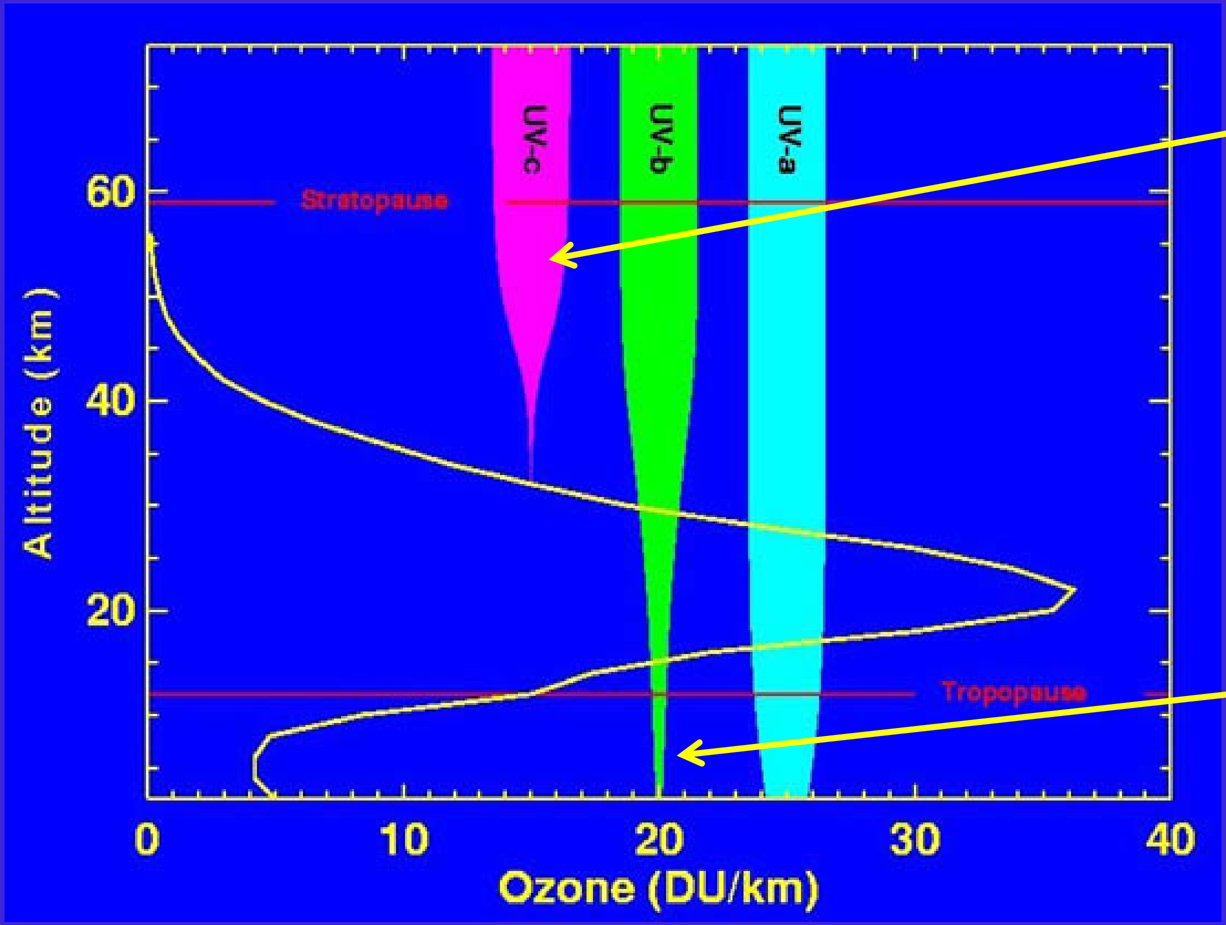
High altitude "cirrus" clouds

And throughout the troposphere where it is relatively humid (formed when air cools)



Composition has important implications for life on Earth

UVc and UVb are harmful for DNA



Ozone (and some other gases) absorb all UVc before it reaches surface

Ozone absorbs most UVb before it reaches surface, but a little does reach the surface, which can injure plants and animals

Mixing Ratios (DJ Pages 1-2)

The most interesting and chemically important molecules in the atmosphere represent the rest of the 0.04%. Note – this is such a smaller percentage that in order to express the value as a number that is one or larger, we will multiply by a value of 1 million (1,000,000 = 10^6).

$$0.04\% = 0.0004 = 400 \times 10^{-6}$$
$$= 400 \text{ “parts per million (ppm)”}$$

What molecules make up this very small remaining fraction 0.04%?

CO_2 ~ 390 ppm (0.0390%)
CH_4 ~ 1.8 ppm (0.00018%)

The remaining gases are < 1 ppm, so we multiply by a billion (10^9)

N_2O ~ 300 ppb (0.0000300%)
CO ~ 100 “parts per billion (ppb)”
O_3 ~ 30 - 60 ppb

Back to the Atmosphere

TABLE 3-2

Major Constituents of Earth's Atmosphere Today

Name and Chemical Symbol	*Concentration (% by volume)*
Nitrogen, N_2	78
Oxygen, O_2	21
Argon, Ar	0.9
Water vapor, H_2O	0.00001 (South Pole)–4 (tropics)
Carbon dioxide, CO_2	0.037*

*In 2002

Roles of some gases in the atmosphere (page 6-10)

N_2 – at 78%, most abundant constituent in atmosphere

78% = 78 molecules of N_2 for every 100 total molecules (78/100)

The nitrogen atom is an important element for life, but in the form N_2, it is very inert because N_2 has a triple bond, so is hard to break apart

N_2 will be the ultimate source of important trace species like nitrogen oxides (NO, NO_2, … HNO_3) and ammonia (NH_3)

Bacteria will have an important 'natural' role in the chemistry of nitrogen, as will lightning

Roles of some gases in the atmosphere (page 6-10)

O_2 – at 21%, formed by photosynthesis , second most abundant, but chemically more reactive than N_2,

21% = 21 molecules of O_2 for every 100 total molecules (21/100)

The source of O atoms for ‘oxidation’ of other molecules, thus being critical in formation of ozone, nitrogen oxides (NO, NO_2, … HNO_3), organic acids (CH_3OOH)

Responsible for our “oxidizing” atmosphere – reduced compounds like methane (CH_4) are removed from the atmosphere

Lots of O_2 in the atmosphere – we don’t need to worry about losing it, even if we burn all the organic mass on surface

Roles of some gases in the atmosphere (page 6-10)

Ar – only 0.9% or 9 molecules of O_2 for every 1000 total air molecules (9/1000)

Formed by radioactive decay of potassium in rocks ($^{40}K40 \rightarrow {}^{40}Ar$) and really has no where to go, so it slowly builds up over time (very important for geologists, but not much to do with atmospheric chemistry)

Minor gases

TABLE 3-3

Important Atmospheric Greenhouse Gases

Name and Chemical Symbol	*Concentration (ppm by volume)*
Water vapor, H_2O	0.1 (South Pole)–40,000 (tropics)
Carbon dioxide, CO_2	370
Methane, CH_4	1.7
Nitrous oxide, N_2O	0.3
Ozone, O_3	0.01 (at the surface)
Freon-11, CCl_3F	0.00026
Freon-12, CCl_2F_2	0.00054

Note – now 400 ppm and still rising

The minor gases (page 8-10)

Water vapor – H_2O – we treat this separately, not because it isn't important, but because it is highly variable, depending on temperature, winds, and precipitation. We don't do much to control water directly, but we may have an influence on water vapor indirectly, by affecting climate, building dams, irrigating, etc.

H_2O will be important as a source for the OH radical, a very reactive specie in the atmosphere that is important in the oxidation of many other gases (see DJ Pages 199-201). OH is also important in smog formation and ozone depletion (DJ Pages 169-170).

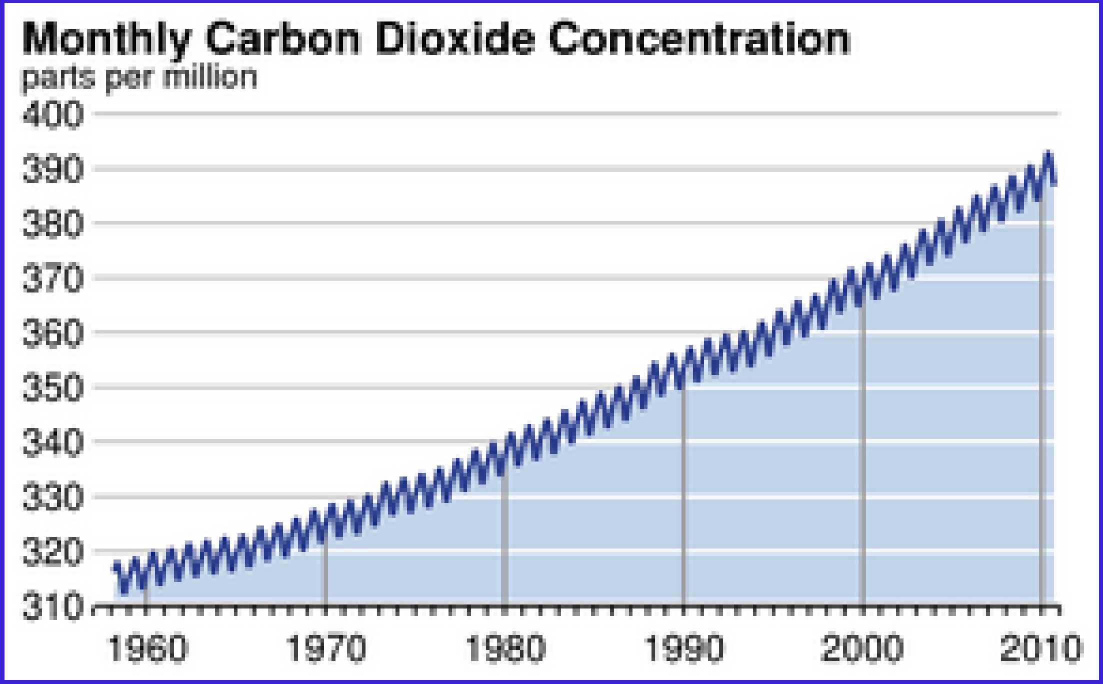
Liquid water is important in the formation of particles, and for dissolving other molecules in particles and rain (DJ Pages 7-9).

The minor gases (DJ Pages 93-95)

CO_2 – Was about 270 parts in one million (270 “ppm”) in the late 1800s, but has been rising since then due to combustion of fossil fuels. In 2014 the mixing ratio first hit 400 ppm (400/1,000,000) = 0.04% at the remote measuring site on Mauna Loa, Hawaii. (**see note)

Removed by photosynthesis and dissolving in water and weathering

Important for climate, but limited role in chemistry (will have small effect on the acidity of rain)



** even though Mauna Loa is a volcano that emits CO_2, any times these emissions are detected at the CO_2 monitoring station they are removed from the record so that only clear air measurements are reported

The minor gases - Methane

CH_4 – methane is presently 1.8 parts per million and rising due to combustion of fossil fuels (1.8/1,000,000) = 0.00018%.

The 2nd-most important anthropogenic greenhouse gas. Although it is 200 times smaller in abundance compared to CO_2, it absorbs at infrared wavelengths that usually pass directly from the surface to space (called a 'window'), so it has a higher trapping efficiency than CO_2.

Can only coexist with O_2 if there is a large source. This is because CH_4 is oxidized ('destroyed') in an oxygen-rich atmosphere (we will see how it reacts with OH later – see page 65 – so that it has a 'lifetime' in the atmosphere of about 9 years)

Photochemical Smog (DJ Pages 232-234)

Tends to be a mixture of reactive gases (like ozone) and particles (“aerosols” or “particulates”, such as can be seen as “haze” in this phot of Denver taken during a temperature inversion in winter

Aerosols (DJ Pages 144-146)

(suspension of particles in air)

For now, note that there are three main ‘modes’ of particles suspended in air

- *Course* mode – particles larger than about 1 micrometer (μm) in diameter. Usually suspended by mechanical processes (e.g. windblown dust)

- *Fine* mode – particles between ~0.05-1 μm. Also called accumulation mode. Usually produced by condensation of water and other volatile materials on smaller particles (something like condensation, but better called *deliquescence* when water and sticking and dissolution on when talking about other species. This mode is responsible for *haze* (e.g. poor visibility).

Aerosols

(suspension of particles in air)

Ultrafine mode – smaller than 0.05 μm, formed exclusively from condensation (e.g. new particle growth). *Condensation nuclei* (CN) are particles that are particularly good at aiding in the formation of larger particles, and *cloud condensation nuclei* (CCN) are particles that eventually form water droplets. Usually small particles (~ few nm) form by homogeneous nucleation ("out of gas phase into liquid phase") of low-volatility gases like sulfuric acid, ammonia, and nitric acid. This typically requires neutralization (that is, positive charges, other than water, equal negative charges).

But particles are pretty complex, and there really isn't a simply way to classify them (doesn't mean we can't try!)

Classification of Particles

“Aerosols” = mixture of gas and solid or liquid