ATOC 3500/CHEM 3151
Air Pollution Chemistry
Lecture 1

Reading: Pages 1-5, 6-8, 8-10

The first few weeks of the course will consist of online lectures linked to reading material in the textbook. Page numbers will guide you to the proper pages in the textbook “Atmospheric Chemistry: Ann M. Holloway and Richard P. Wayne” Supplemental material can be found in an online textbook by Daniel Jacob of Harvard University, with pages labeled as “DJ-##”).

http://acmg.seas.harvard.edu/publications/jacobbook/index.html

At various points problems related to the content will be introduced. These problems are available in Word format for download at the main website:

http://storm.colorado.edu/~toohey/A3500-2018.html

Answers can be uploaded to Dropbox folders on D2L

“Atmos” = vapor + “sphaira” = ball

What is Air?

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").

Chapter 1 – Basics of the Atmosphere

P 1-2

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 minute trace amounts can have important roles. In a number of cases (like the Antarctic Ozone Hole), a particular bromine molecule that is present in only 10 parts out of 1 trillion total molecules (also ‘10 parts per trillion’, or $10x10^{-12}$) is more important than a gas like CO_2 that is present at tens of thousands of times the amount.

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

Chapter 1 – Atmospheric Structure

P 2-5

Because the atmosphere is compressible, we will need an equation that describes the pressure and density with altitude. Obviously, the higher one goes in the atmosphere, the lower the pressure and density. The weight of air above a particular altitude determines the pressure at that altitude. Therefore, the highest pressure is at sea level (~1013 millibars) and pressure drops logarithmically with altitude (we will see this later in Figure 2.1).

Gases tend to mix relatively quickly (~days to years) at altitudes up to about 100 km, so below 100 km we don't need to worry about "fractionation" or gravitational "settling." But we do need to consider chemical reactions that change concentrations of different compounds, and we need to consider condensation and precipitation (in the case of water vapor).

Problem 1 - Surface Pressure in Different Units

http://storm.colorado.edu/~toohey/A3500-PS1.docx

Chapter 1 – Atmospheric Structure

We will also find that temperature changes dramatically with altitude. This is seen in Figure 1.1 on Page 3. This is an important figure to examine. Problems in atmospheric chemistry can often be segregated by temperature, pressure, and amounts (and type) of sunlight.

For example, near the surface, where pressure is highest and temperatures are relatively warm, in daylight chemical reactions can be rapid, and with the right mix of chemicals a toxic molecule called “ozone” can form. Although ozone is important for shielding the surface from harmful ultraviolet light, it is also harmful to breathe in high enough amounts.

In this class, we will discuss this chemistry of ozone formation (called “photochemical smog chemistry”) in more detail.

Chapter 1 – Atmospheric Structure

We also find that chemistry influences the temperature of the atmosphere. This is shown in the figure on the next slide.

So the chemical composition of the atmosphere and its thermal structure cannot be separated – they are inextricably linked.

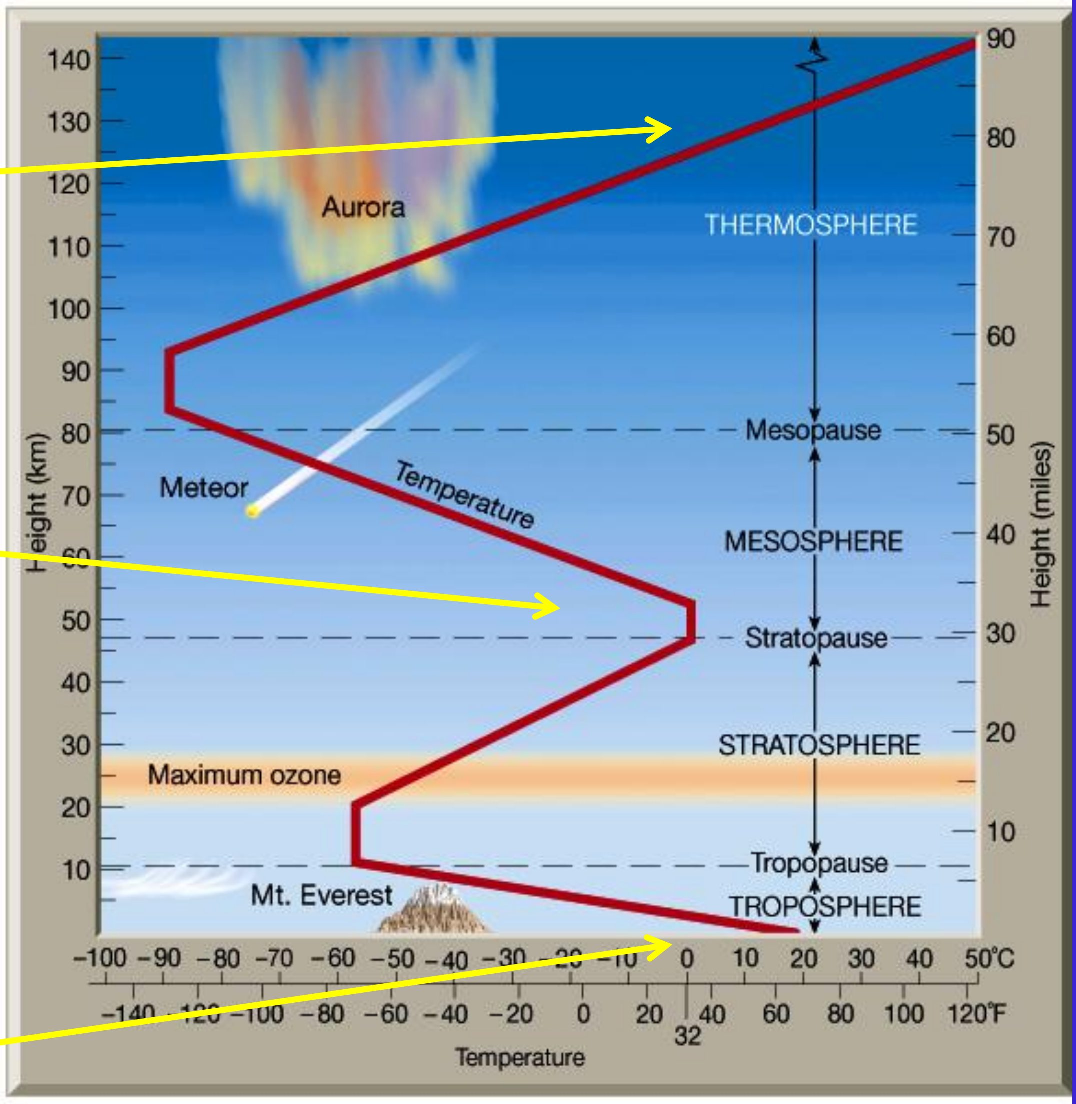
When we talk about various problems in the atmosphere, such as "urban smog," "ozone depletion," and "acid rain," we will often label the problems in terms of geographic region or altitude where they most frequently occur. We will also talk about various layers of the atmosphere, such as the lowermost layer (the "troposphere") and the stratified layer from about 15 to 50 km, called the "stratosphere." There are different chemistries in these different layers, but the methods for understanding the chemical reactions that occur are similar.

Vertical structure of the atmosphere – the roles of chemistry and sunlight

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



Problem 2 – The Mass of the Atmosphere

On page 2 of the textbook, the following statement is made:

The total mass of Earth's atmosphere is around 5 x 10^{18} *kg.*

Let's figure out how this number is determined. Clearly, no one has weighed the entire atmosphere. But knowing that pressure is "weight per unit area", we can use the average surface pressure of the atmosphere and the total surface area of the Earth to calculate the mass.

http://storm.colorado.edu/~toohey/A3500-PS2.docx

Atmospheric Composition

Ultimately, a class dedicated to atmospheric chemistry deals with a variety of chemical compounds (or “constituents”) that occur in the atmosphere for a variety of reasons. Some occur naturally, some are emitted by human activities and that we call “primary pollutants,” and some are produced by a combination of reactions between naturally occurring compounds and these primary pollutants, and these we call “secondary pollutants.”

An important aspect of the chemistry of various constituents in the atmosphere, and, hence, a key to their importance to air pollution and other environmental issues, is their abundances or “concentrations.” We will have several different ways to describe these concentrations, and we will categorize various compounds as “major” and “minor” constituents. One important quantity we will use is the “average molecular weight” of the atmosphere, which is primarily determined by the major constituents nitrogen (N_2), oxygen (O_2), and argon (Ar).

Back to the Atmosphere

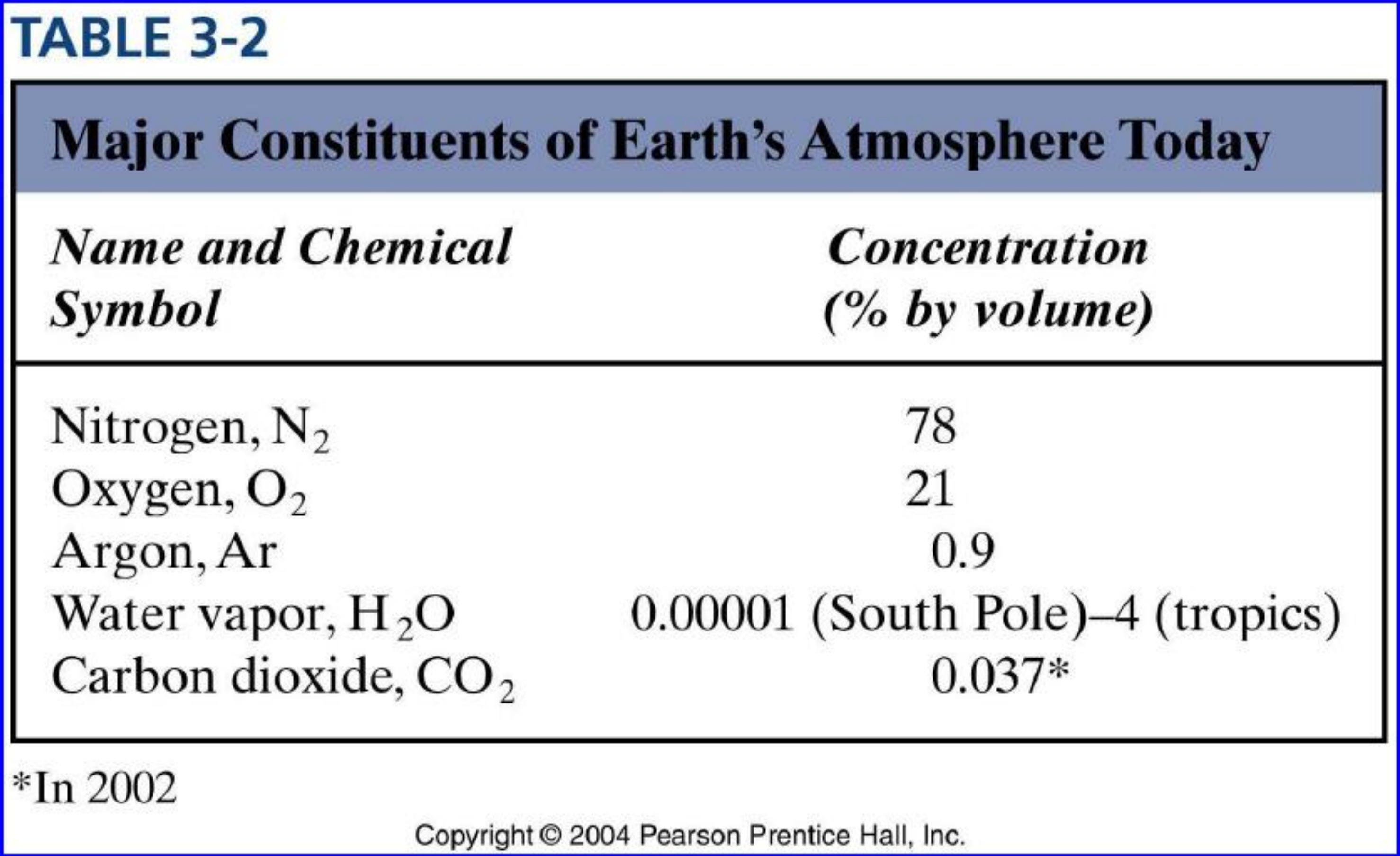


TABLE 3-2

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 by oxygenated species

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 ($^{40}K \rightarrow {}^{40}Ar$) 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)

Atmospheric Composition

An important quantity we will use is the “average molecular weight” of the atmosphere, which is primarily determined by the major constituents nitrogen (N_2), oxygen (O_2), and argon (Ar).

Problem 3 – The average molecular weight of the atmosphere

http://storm.colorado.edu/~toohey/A3500-PS3.docx

On Mixing Ratios
Page 12-13 (DJ-01-02)

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 ($1{,}000{,}000 = 10^6$).

$$0.041\% = 0.00041 = 410 \times 10^{-6}$$
= 410 "parts per million (ppm)"

What molecules make up this very small remaining fraction 0.041%?

CO_2 ~ 400 ppm (0.0400%)
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

Particles and clouds also impact atmospheric composition

This is a picture of polar stratospheric clouds from Kiruna, Sweden. These clouds in the stratosphere made of ice and responsible for altering the normal chlorine chemistry in the ozone layer, thereby leading to ozone holes that are seen over Antarctica and the Arctic.

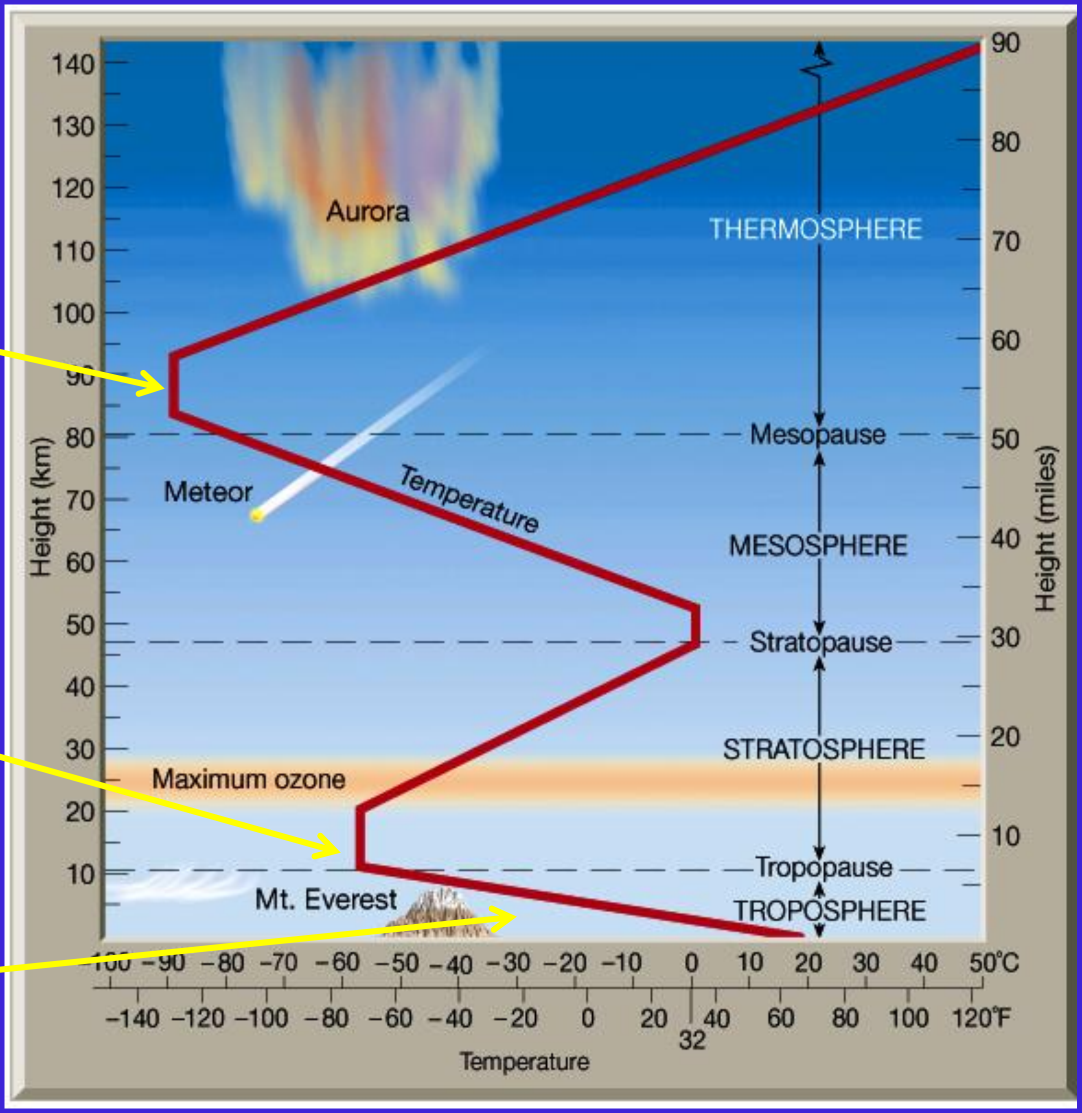
Where do clouds form?

In cold regions at high altitudes:

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

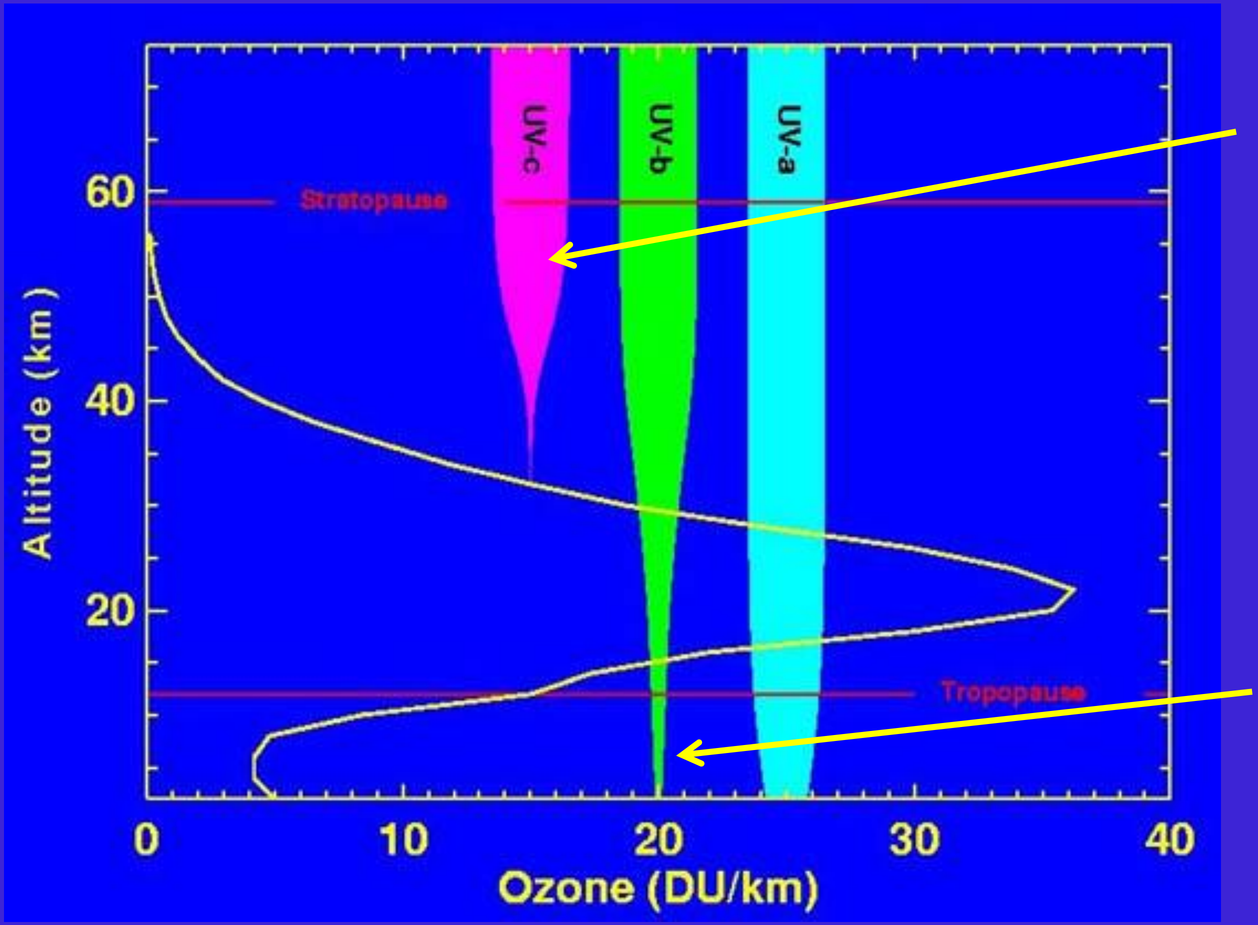
High altitude “cirrus” clouds

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

Minor gases

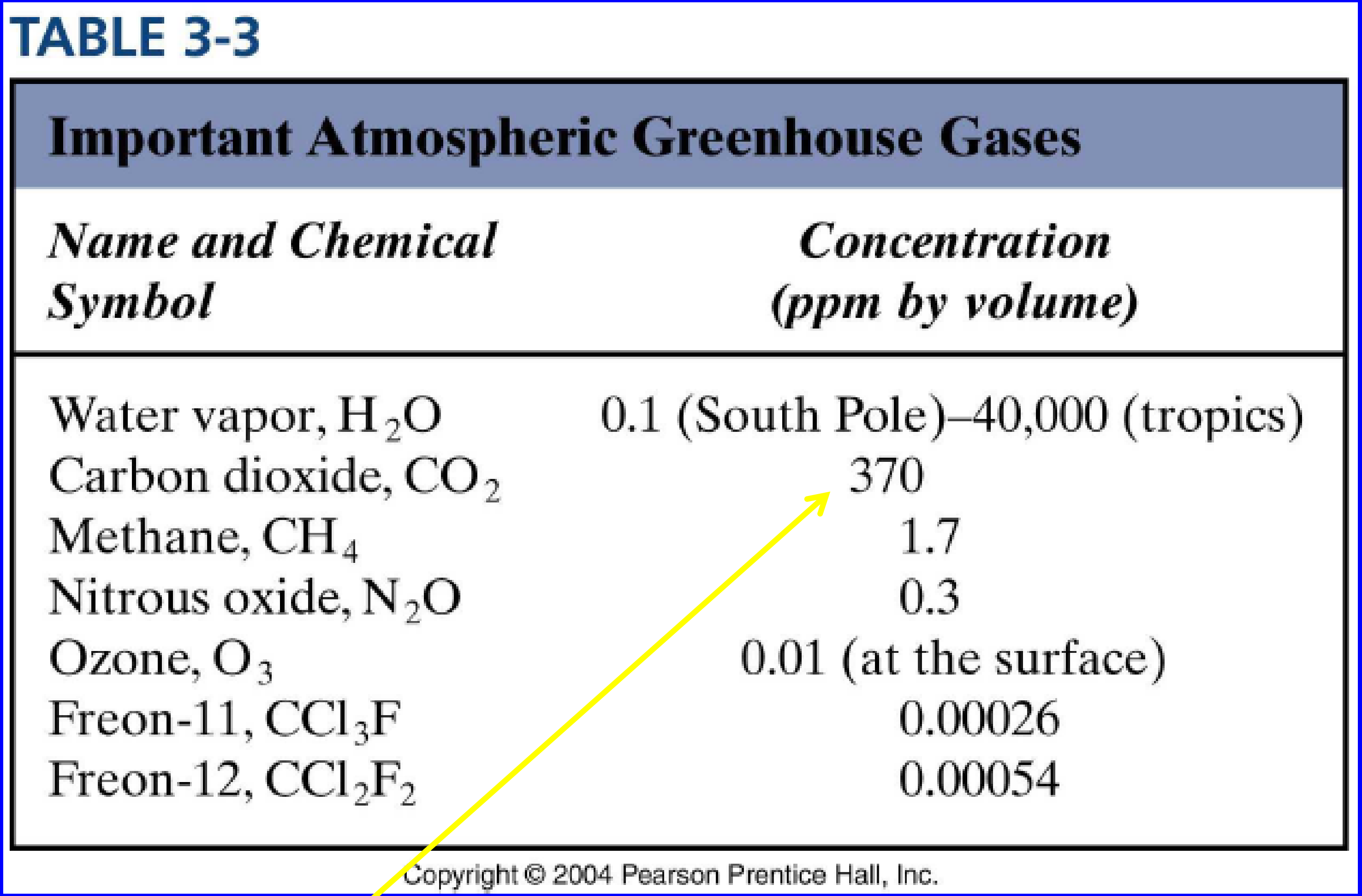


TABLE 3-3

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 over 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.

It 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 page 101). OH is also important in smog formation and ozone depletion.

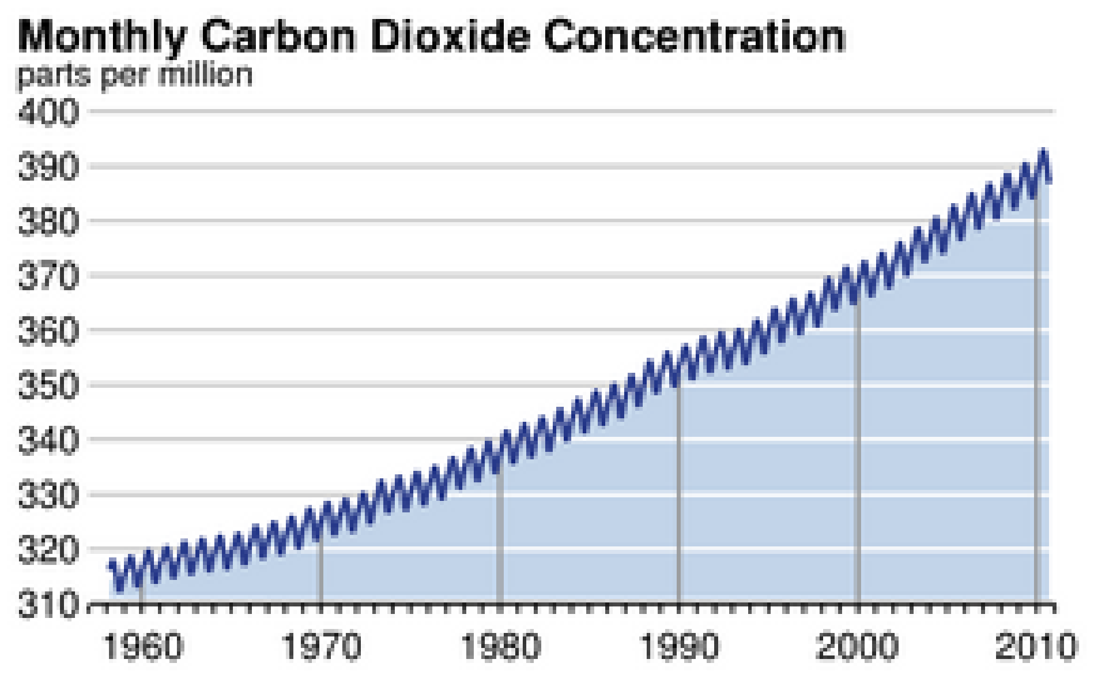
Liquid water is important in the formation of particles, and for dissolving other molecules in particles and rain.

The minor gases (page 8-10)

CO_2 – presently over 400 parts in one million (400 “ppm”) and rising due to combustion of fossil fuels (400/1,000,000) = 0.0400%

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)



The minor gases (page 8-10)

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)

Problem 4 – Mixing Ratios

http://storm.colorado.edu/~toohey/A3500-PS4.docx