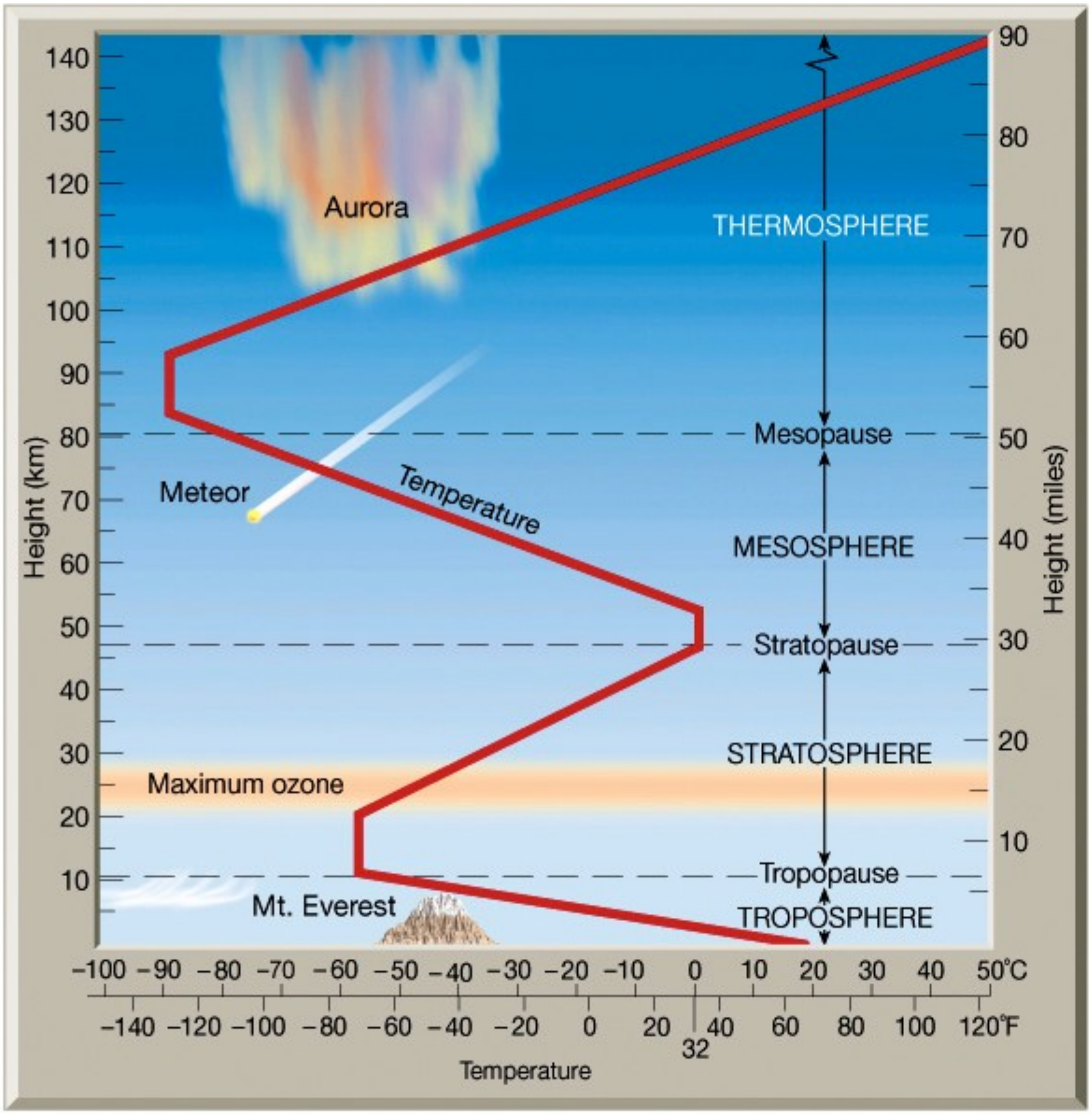
The Atmosphere

August 30, 1984

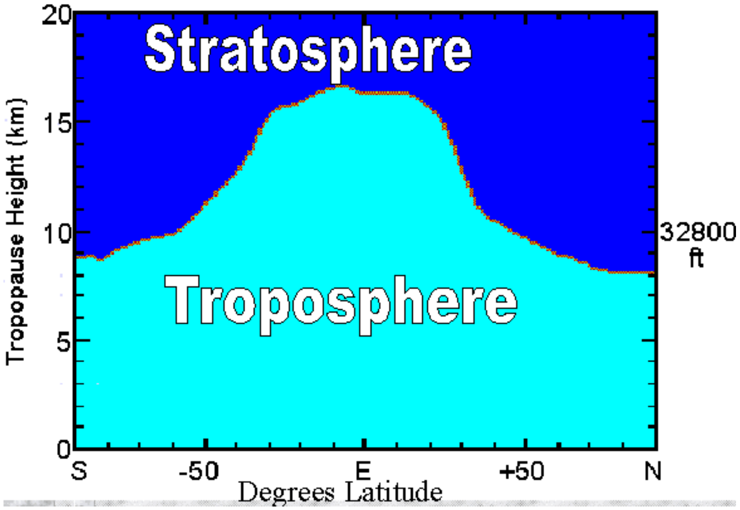
August 8, 1991

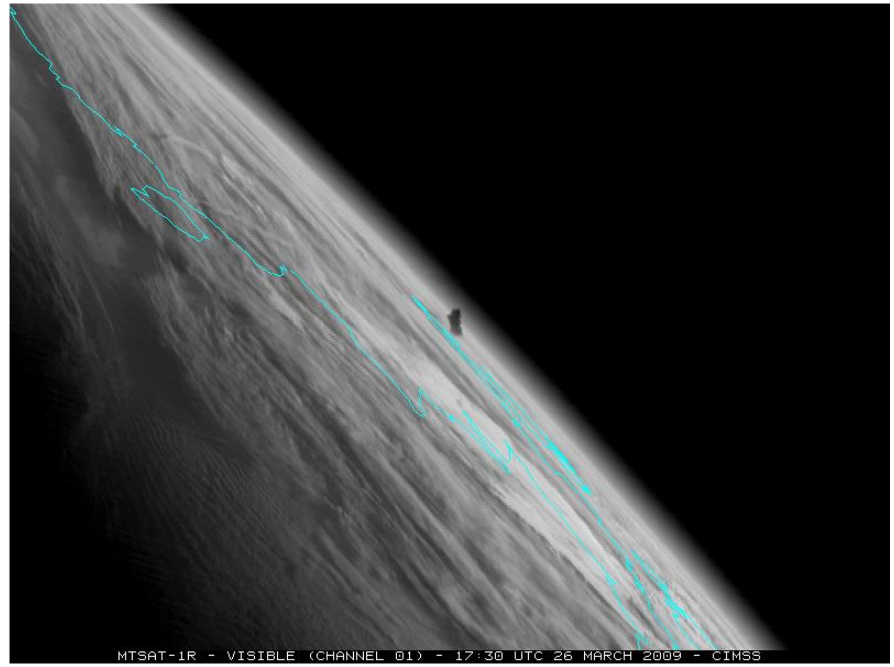
Atmospheric structure

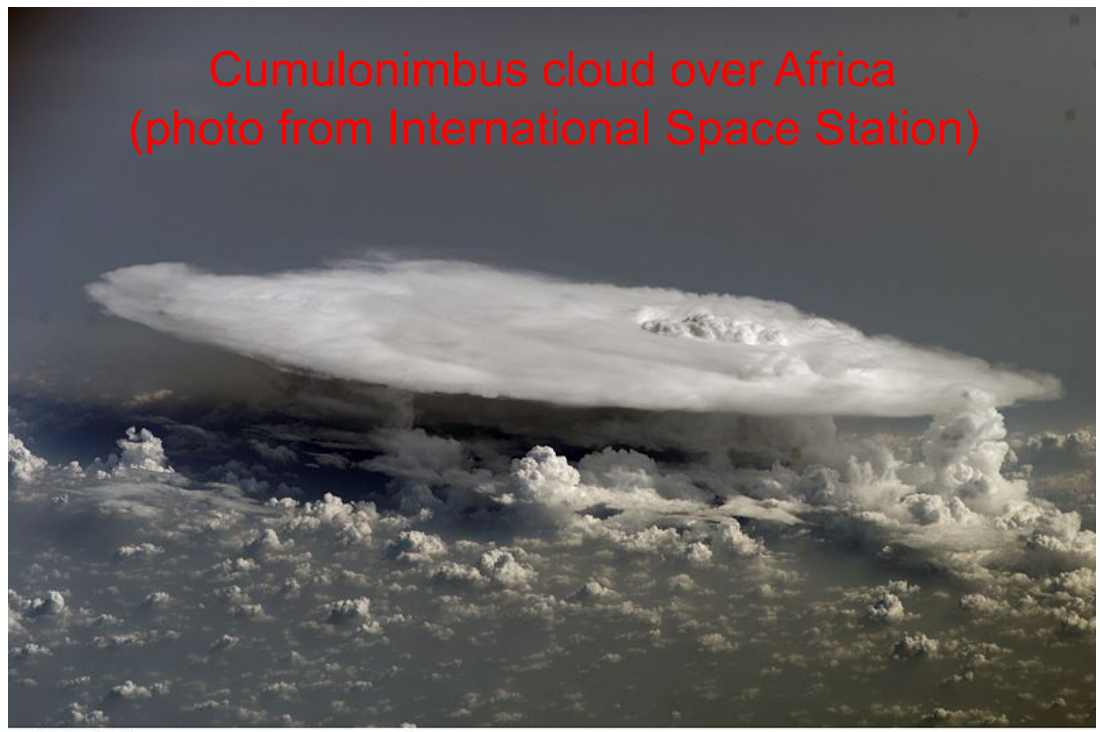


- Atmospheric layers defined by changes in temperature
- Troposphere – contains 75% of atmospheric gases; temperature decreases with height
- Tropopause – boundary between troposphere and stratosphere; location of the jet stream
- Tropopause altitude varies from ~8 km (Poles) to ~17 km (Tropics)
- Stratosphere – contains the ozone layer, which causes the temperature to increase
- Thermosphere: highly energetic solar radiation (UV, X-rays) absorbed by residual atmospheric gases

Tropopause altitude







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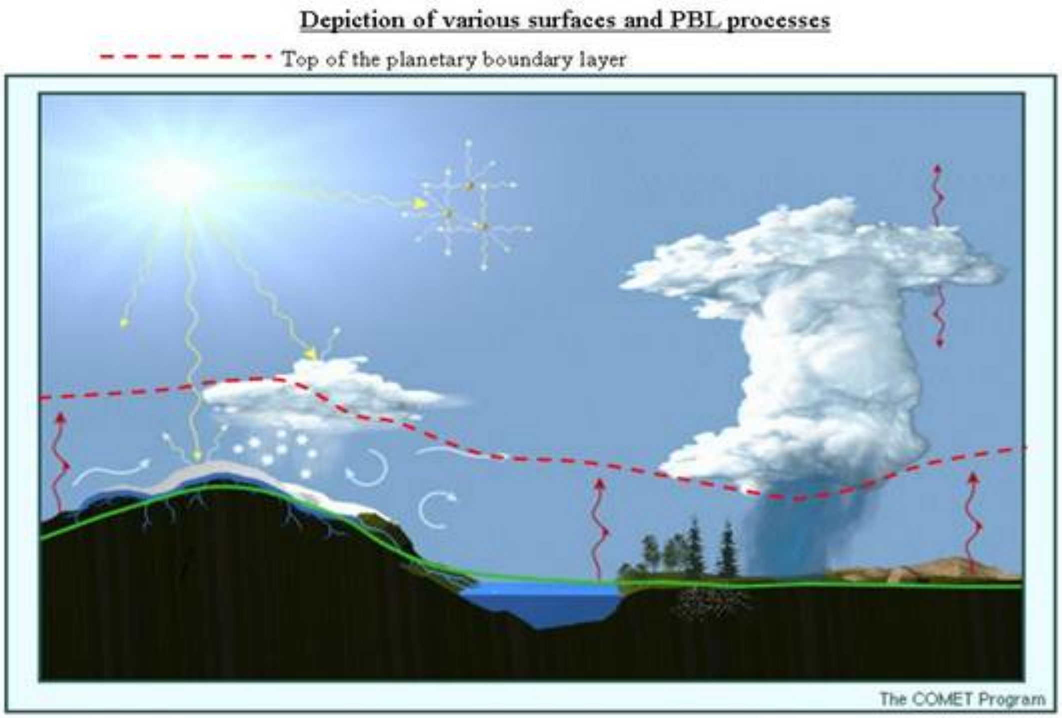
- Tropopause altitude is dependent on latitude – it is highest in the tropics where convection is strong
- The tropopause is not a 'hard' boundary – it can be defined thermally, dynamically or chemically

Planetary boundary layer (PBL)



PBL height
300 m – 3 km
• Influenced by convection
• Varies diurnally

• The PBL is the lowest part of the atmosphere – directly influenced by contact with the planetary surface

• Responds to changes in surface forcing rapidly (hours)

• Quantities such as flow velocity, temperature, moisture show rapid variations (turbulence) and vertical mixing is strong

• PBL winds are affected by surface drag, as opposed to winds in the 'free troposphere' above which are determined by pressure gradients

Atmospheric pressure

Hypsometric equation

$$h = \frac{RT}{g} \ln\left[\frac{P_1}{P_2}\right]$$

h = layer thickness (m)

R = ideal gas constant (8.314 J K^{-1} mol^{-1})

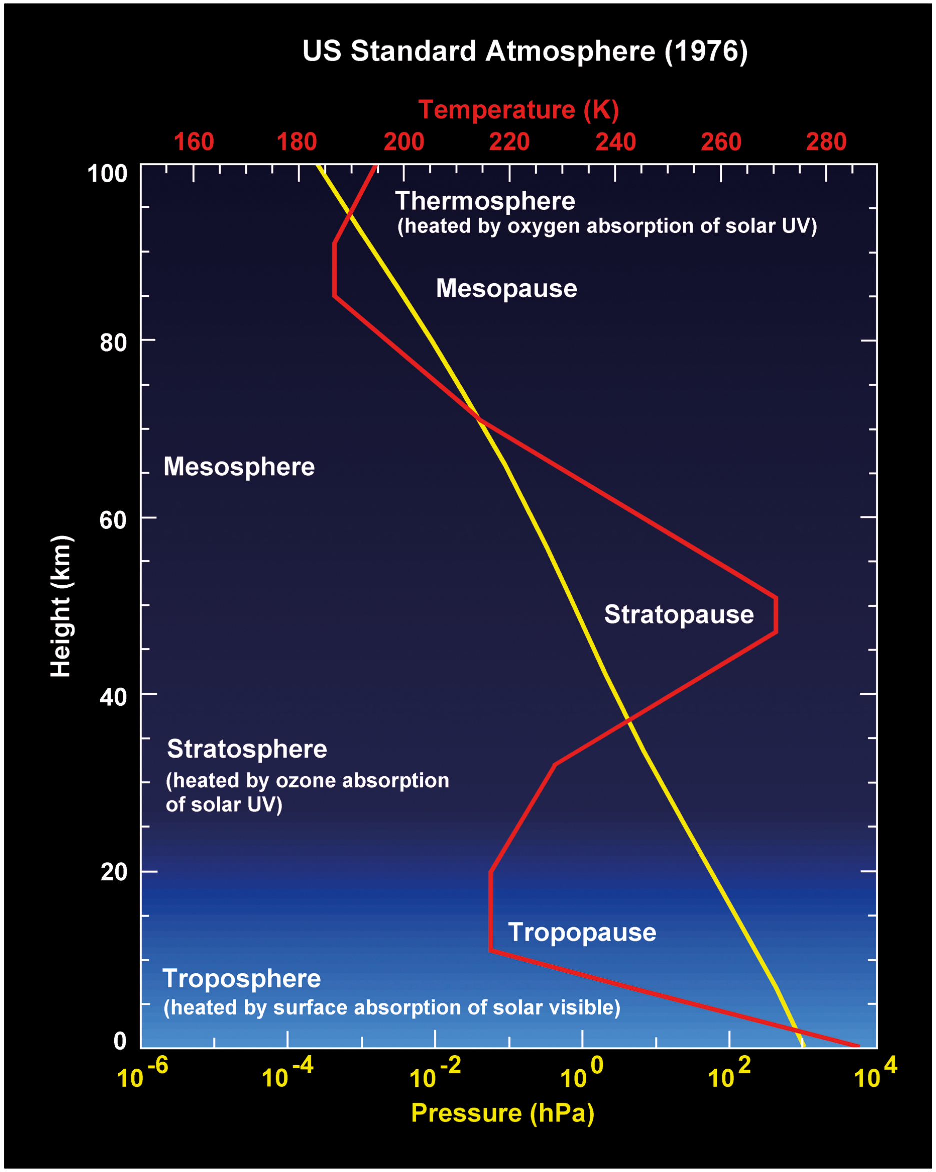
T = temperature (K)

g = gravitational acceleration (9.81 m s^{-2})

P = pressure (Pa)

- Atmospheric pressure is the weight of the gases surrounding the earth. It is a function of height, density and gravity.
- Energy (motion) at the molecular level creates atmospheric pressure and prevents the atmosphere from collapsing on itself
- At ground level it is recorded as 101.32 kilopascals (kPa) ; equal to 14.7 lbs. per sq. inch or 760 mm Hg (also 1 atmosphere, 1 bar, 1000 millibars etc.)
- Atmospheric pressure decreases exponentially with altitude: at 18,000 ft. (~6 km) it is halved and at 33,000 ft., (~11 km) quartered
- Note that in water atmospheric pressure doubles at at a depth of 33 ft

The Standard Atmosphere

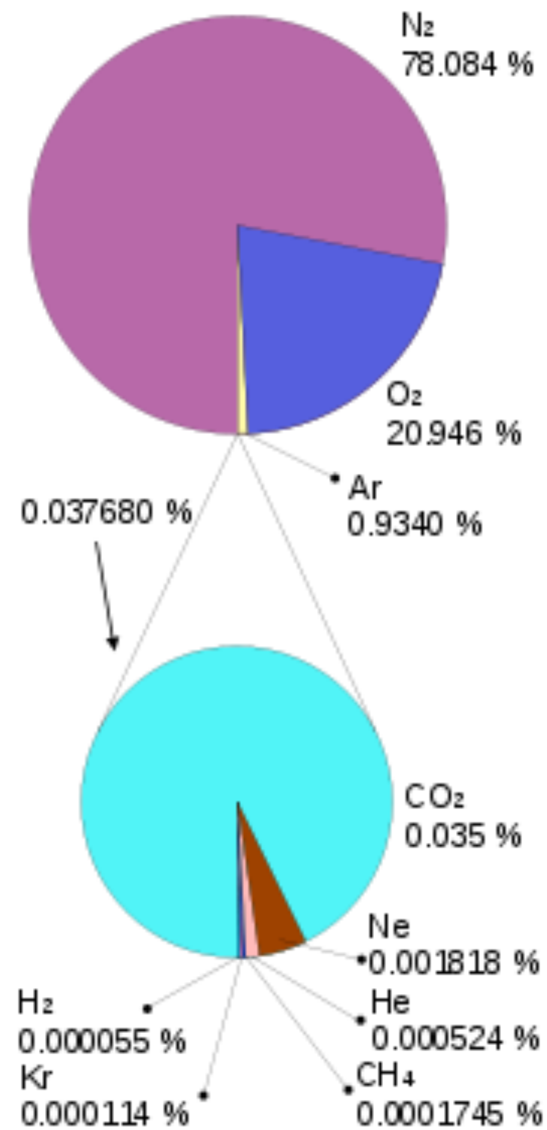


- Standard (or model) atmospheres facilitate comparison of radiative transfer models
- They represent 'typical' atmospheric conditions for a particular region/season
- Used whenever an actual *sounding* (measurement of the atmospheric state) is not available
- At least 7 standard model atmospheres are in common use: *tropical* (warm, humid, high tropopause), *midlatitude summer*, *midlatitude winter*, *subarctic summer*, *subarctic winter*, *arctic summer* and *arctic winter* (cold, dry, low tropopause)

Atmospheric composition

Composition of dry atmosphere, by volume

Nitrogen (N_2)	78% (780,840 ppmv)
Oxygen (O_2)	21% (209,460 ppmv)
Argon (Ar)	0.93% (9340 ppmv)
Carbon dioxide (CO_2)	0.04% (383 ppmv)
Neon (Ne)	0.002%
Helium (He)	0.0005%
Methane (CH_4)	0.0001%
Krypton (Kr)	
Hydrogen (H_2)	
Nitrous oxide (N_2O)	
Ozone (O_3)	0-0.07 ppmv
Water vapor (H_2O)	1-4% at surface



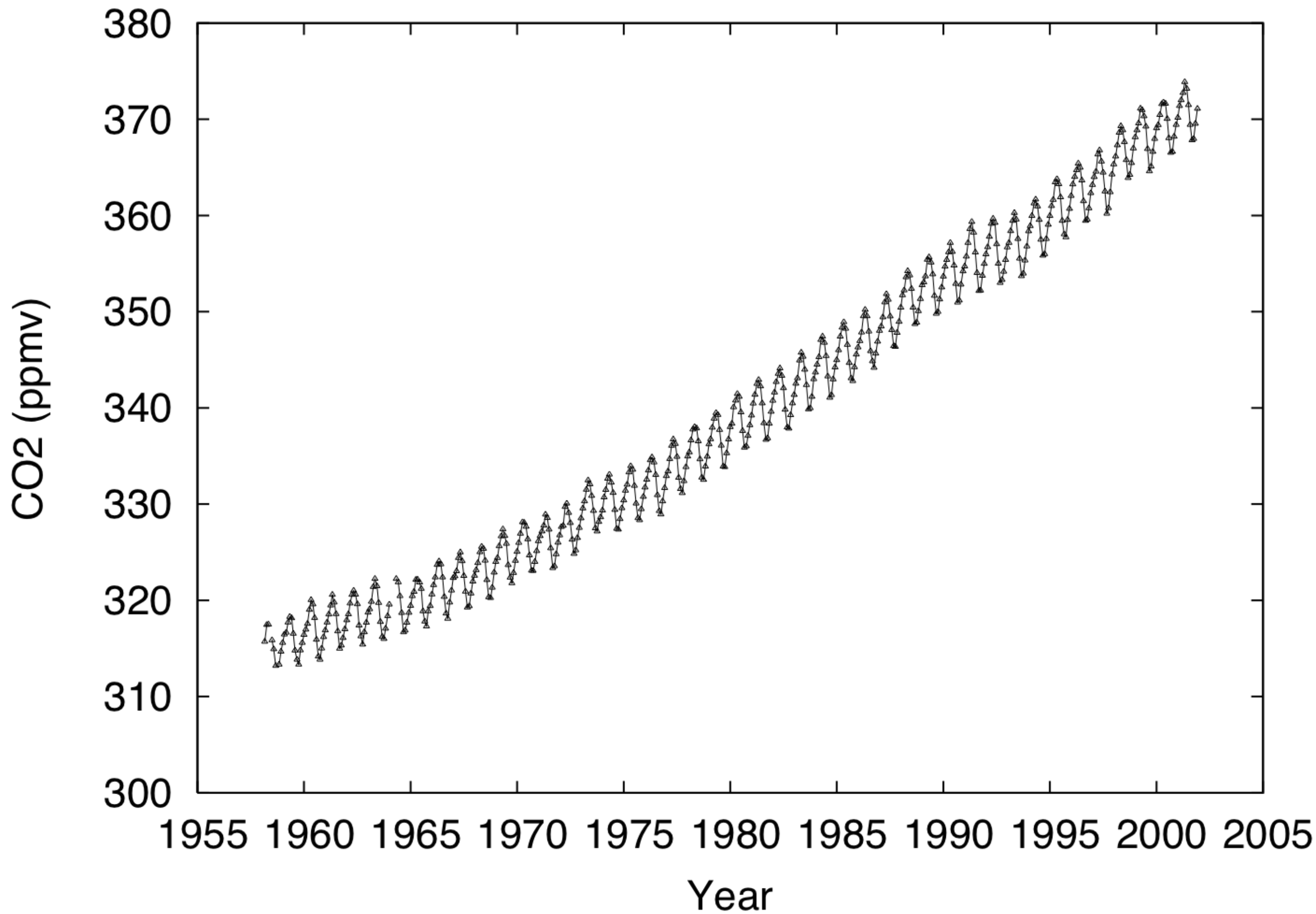
ppmv = parts per million by volume = volume mixing ratio

Trace constituents

Chemical Species	Concentrations	
	mol/mol	Other units
Carbon monoxide	$(0.1\text{-}20)\times10^{-6}$	100 ppb to 20 ppm
Methane	1.72×10^{-6}	1.72 ppm
Ozone	$(1\text{-}100)\times10^{-9}$	1-100 ppb
Nitric oxide (NO)	$(0.005\text{-}1)\times10^{-9}$	5 ppt-1ppb
Nitrogen dioxide (NO2)	$(1\text{-}150)\times10^{-9}$	1-150 ppb
Nitrous oxide (N2O)	310×10^{-9}	310 ppb
Ammonia (NH3)	$(0\text{-}0.5)\times10^{-9}$	0-0.5 ppb
Sulfur dioxide (SO2)	$(1\text{-}100)\times10^{-9}$	1-100 ppb
CFCl3 (Freon 11)	0.2×10^{-9}	200 ppt
CF2Cl2 (Freon 12)	0.35×10^{-9}	350 ppt

Some atmospheric trace gases of environmental significance

CO_2 concentrations



Measurements of atmospheric carbon dioxide at Mauna Loa Observatory, Hawaii
(Keeling curve)

The Ozone Layer

- The stratospheric ozone layer is a consequence of molecular *photodissociation*
- UV-C radiation dissociates molecular oxygen:

$$O_2 + hv\ (\lambda < 0.2423\ \mu m) \rightarrow O + O$$

- The large amount of oxygen in the atmospheric column absorbs most solar radiation at $\lambda < 0.24\ \mu m$ by this mechanism
- The free oxygen atoms from the above reaction then combine with other O_2 molecules to produce ozone:

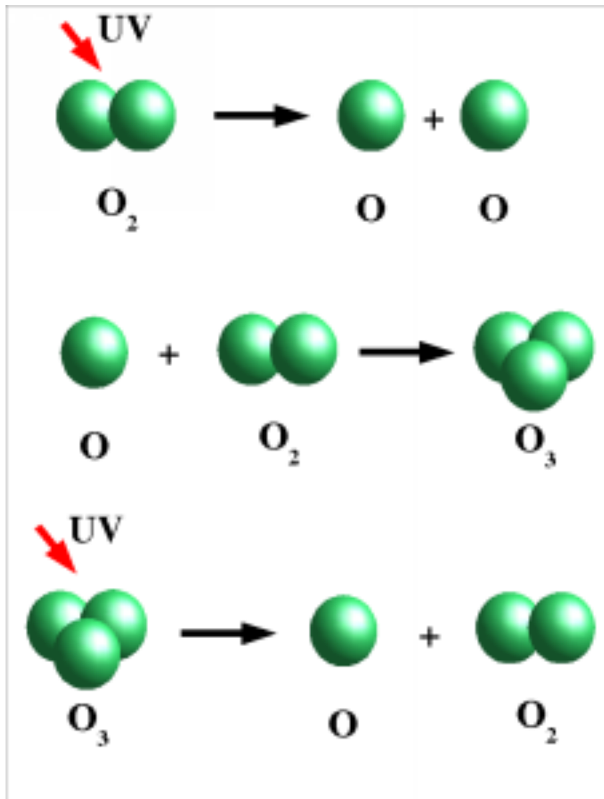
$$O + O_2 \rightarrow O_3$$

- Ozone is then dissociated by UV radiation:

$$O_3 + hv\ (\lambda < 0.32\ \mu m) \rightarrow O + O_2$$

- Ozone is also destroyed by this reaction:

$$O_3 + O \rightarrow O_2 + O_2$$



The Chapman Reactions

The Ozone Layer

• Fortunately for life on Earth, ozone absorbs strongly between 0.2 and 0.31 μm via electronic transitions – removing most UV-B and UV-C not absorbed by O_2

• UV-A radiation ($\lambda > 0.32$ μm) is transmitted to the lower atmosphere

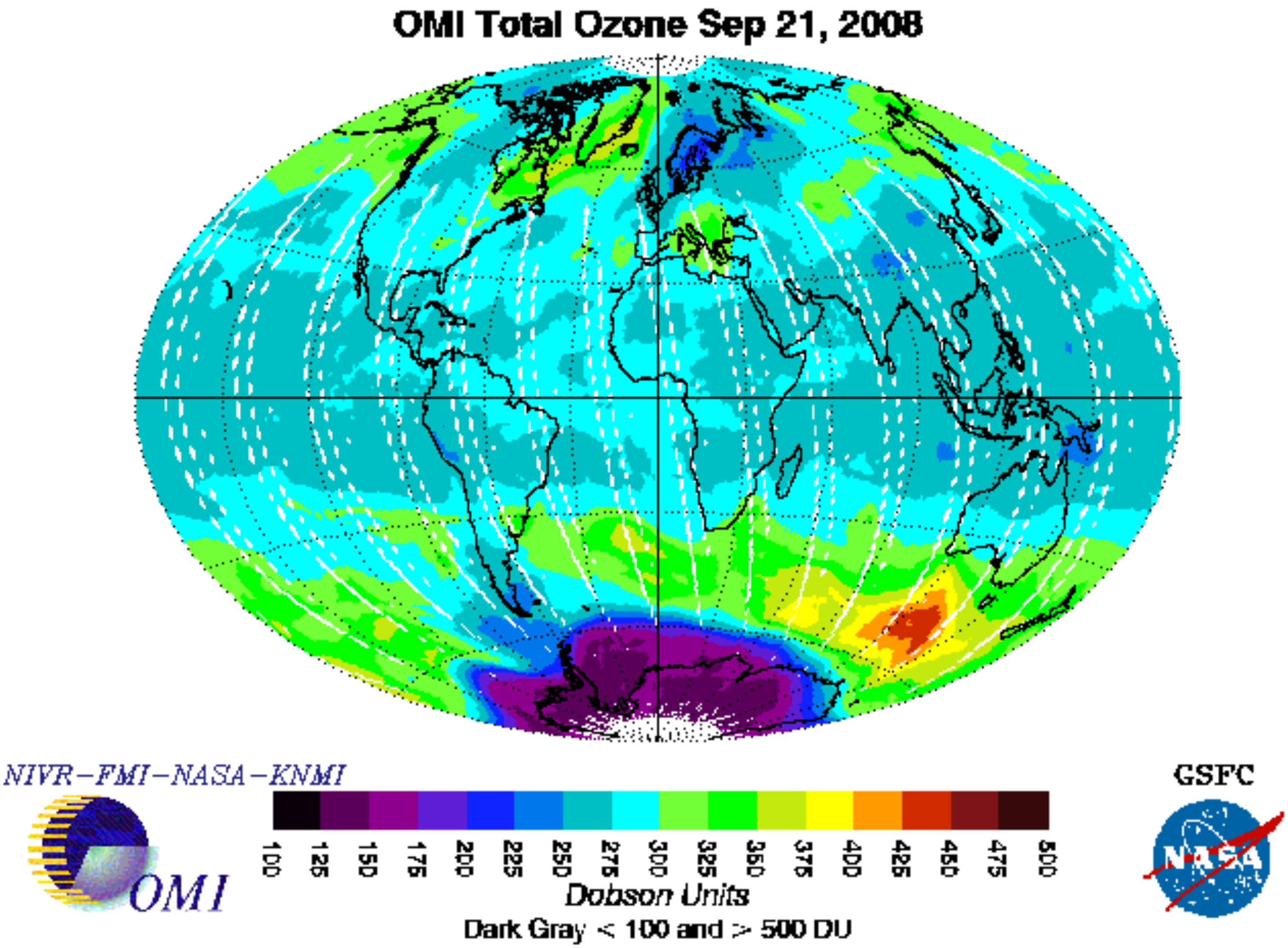
• Plus a small fraction of UV-B (0.31-0.32 μm) – responsible for sunburn

• Widening of this UV-B window (due to ozone depletion) would have serious impacts on life

• Absorption of solar radiation by ozone also locally warms the atmosphere to a much higher temperature than would be possible if ozone was absent – hence the increase in T in the stratosphere

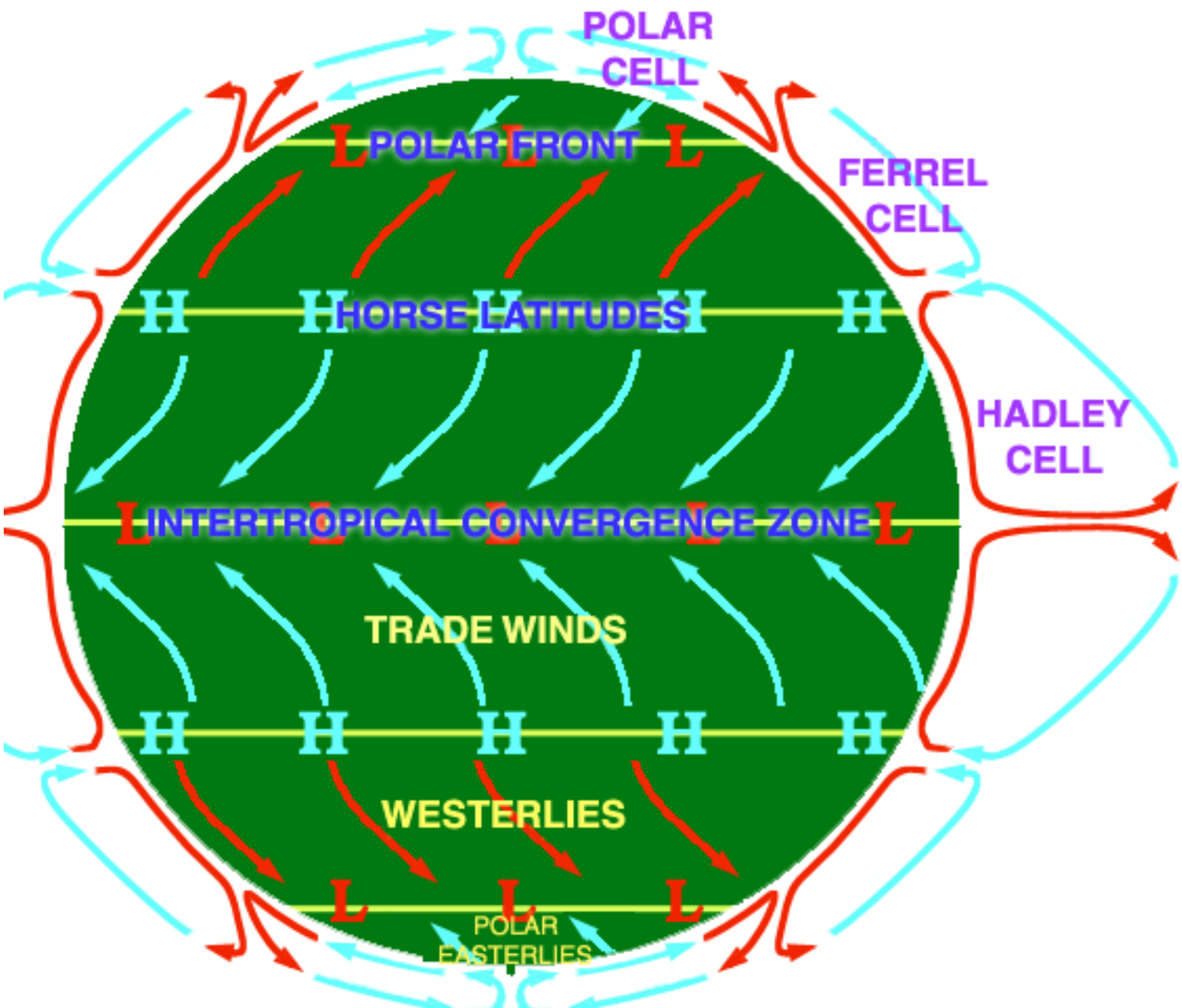
• Hence in an atmosphere without free oxygen, and hence without ozone, the temperature would decrease with height until the thermosphere. There would be *no stratosphere*, and weather would be vastly different...

The Ozone Layer

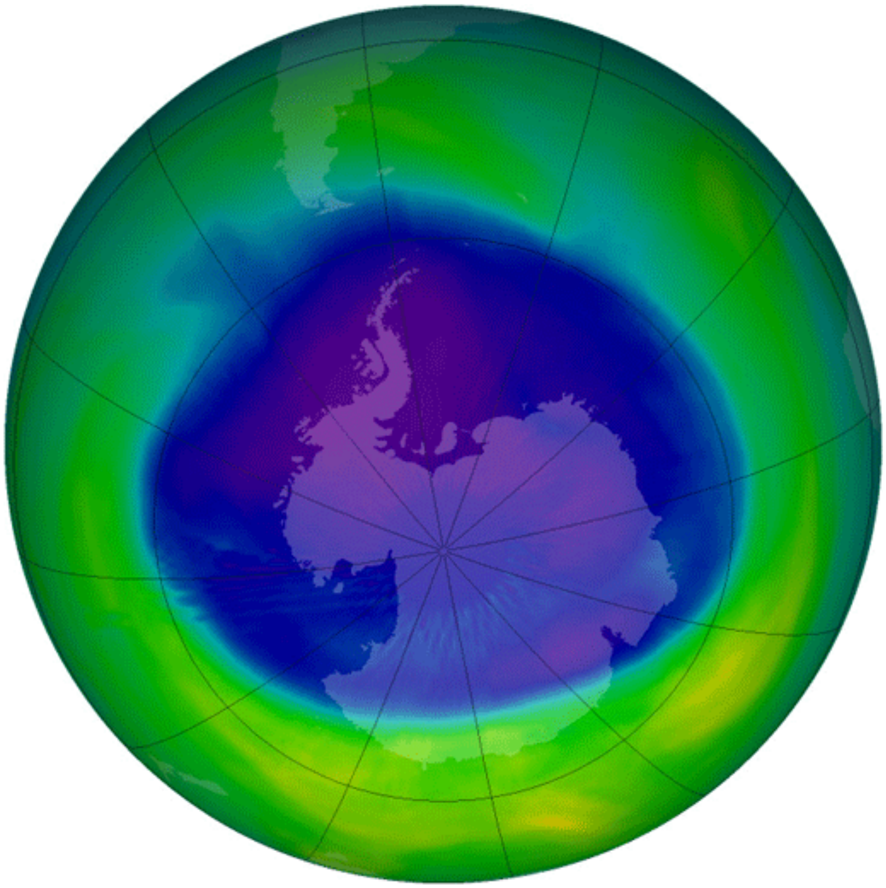


• Most of the ozone production occurs in the tropical upper stratosphere and mesosphere, but the ozone maximum occurs at mid-latitudes

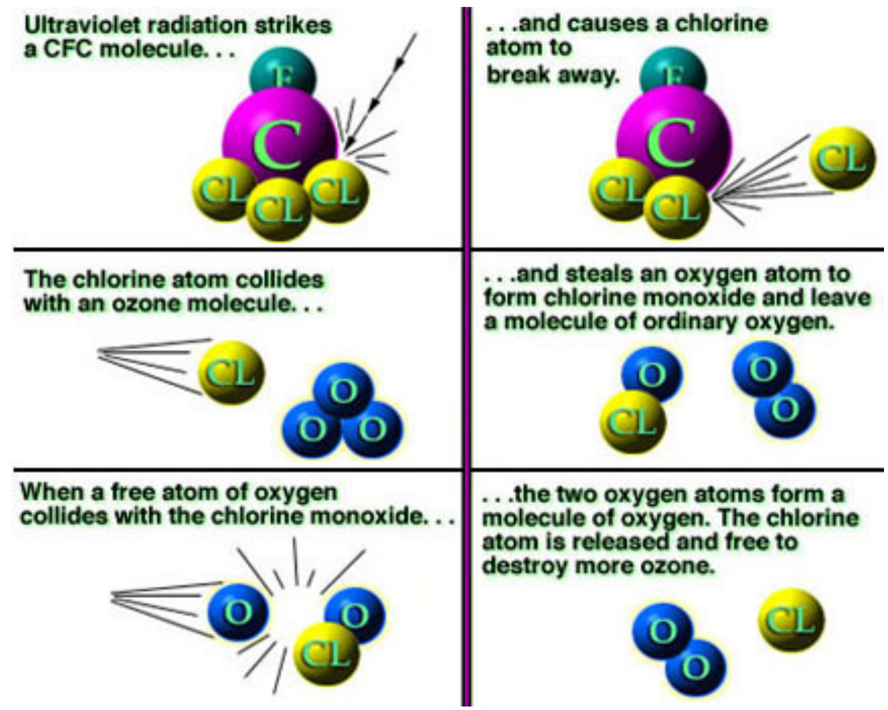
Atmospheric circulation



Ozone hole



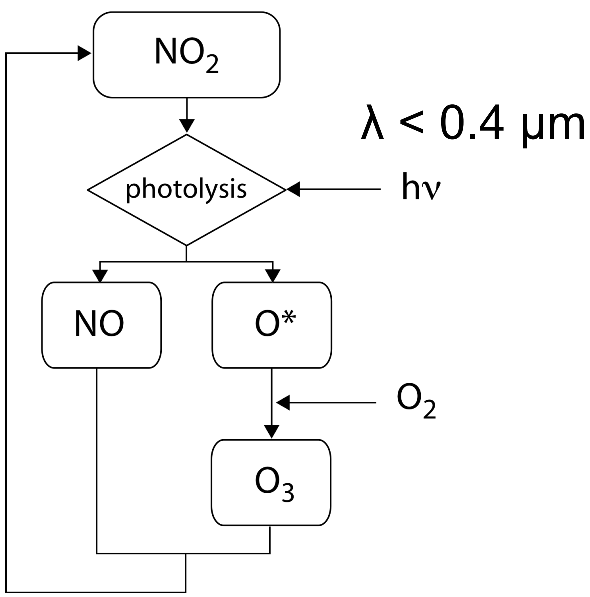
Antarctic ozone hole on Sept 11, 2005
Observed by Ozone Monitoring Instrument (OMI)



- Ozone destruction peaks in the Spring, as UV radiation returns to the polar regions
- Catalyzed by the presence of CFC compounds (which supply chlorine), and by polar stratospheric clouds (PSCs) at very cold temperatures

Ozone is not just in the stratosphere..

- The UV-A radiation that reaches the troposphere is a key player in tropospheric chemistry
- *Photochemical reactions* involving *unburned fuel vapors* (organic molecules) and *nitrogen oxides* (produced at high temperatures in car engines) produce ozone in surface air (tropospheric ozone)
- Ozone is good in the stratosphere, but a hazard in the troposphere (it is a strong oxidant that attacks organic substances, such as our lungs)
- Ozone is a major ingredient of photochemical smog

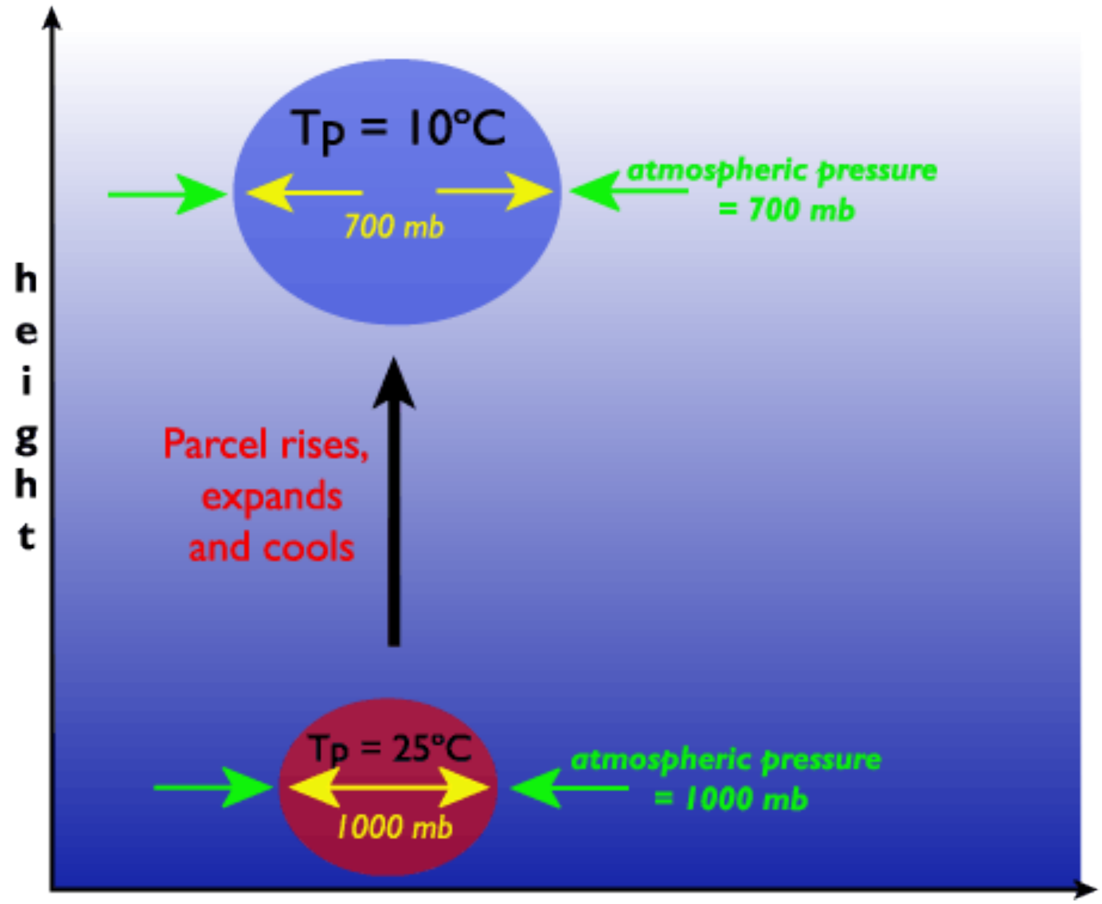


Los Angeles: sunshine (UV) + cars + trapped air = smog

Atmospheric stability

Adiabatic cooling

- As an air parcel rises, it will adiabatically expand and cool
- Adiabatic: *temperature changes solely due to expansion or compression* (change in molecular energy), no heat is added to or removed from the parcel



Atmospheric stability

Dry air – no condensation
Dry adiabatic lapse rate = ~10ºC km^{-1}

Rising air parcel encounters decrease in surrounding pressure and expands.

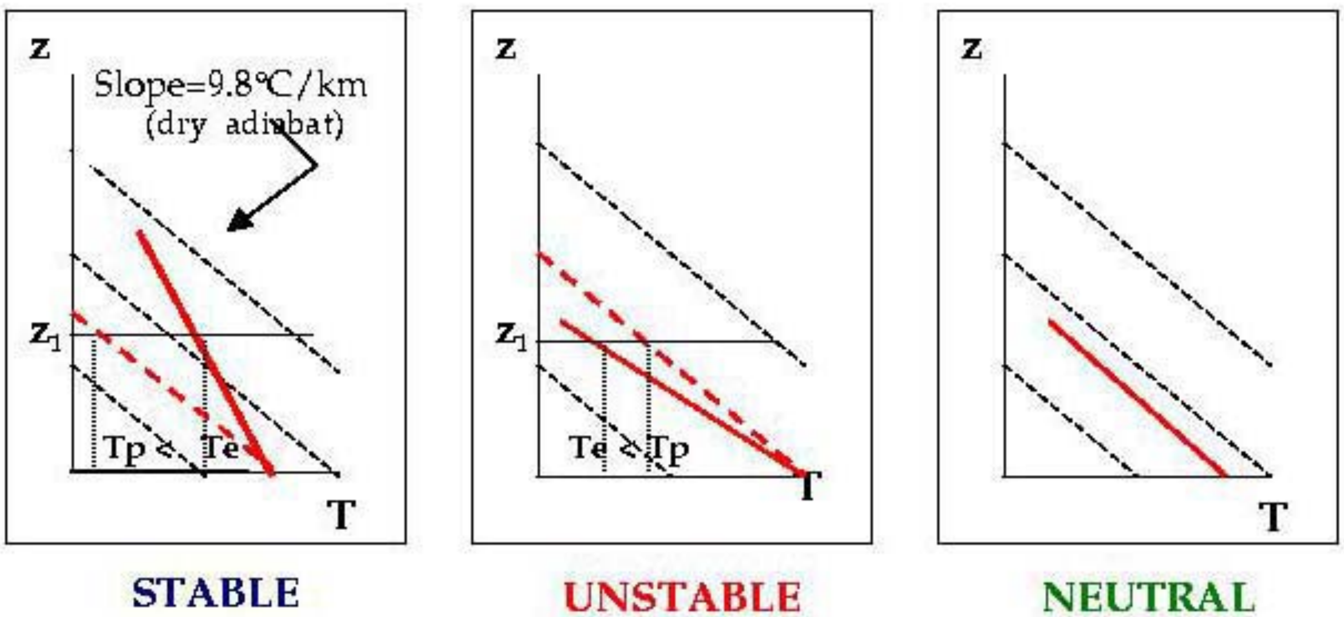
Expansion is adiabatic and implies a decrease in parcel temperature.

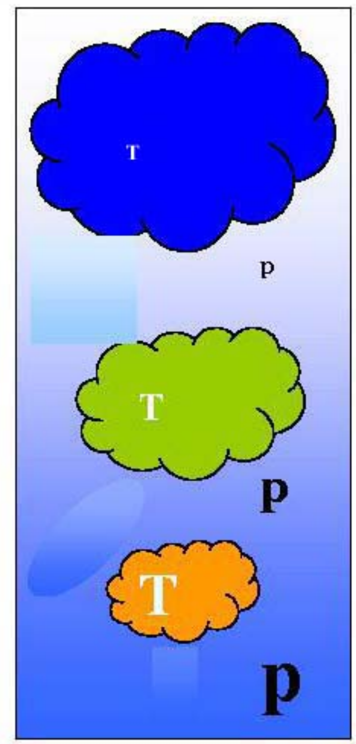
The dry adiabatic lapse rate:

$\Gamma_d = 9.8°C / \text{kilometer}$

Stability of Dry Air

In the diagrams below solid red line is the environmental lapse rate, and dashed red is the dry adiabat for a parcel rising from the surface in that environment. Tp and Te are the parcel and environment temperature at level Z_1.

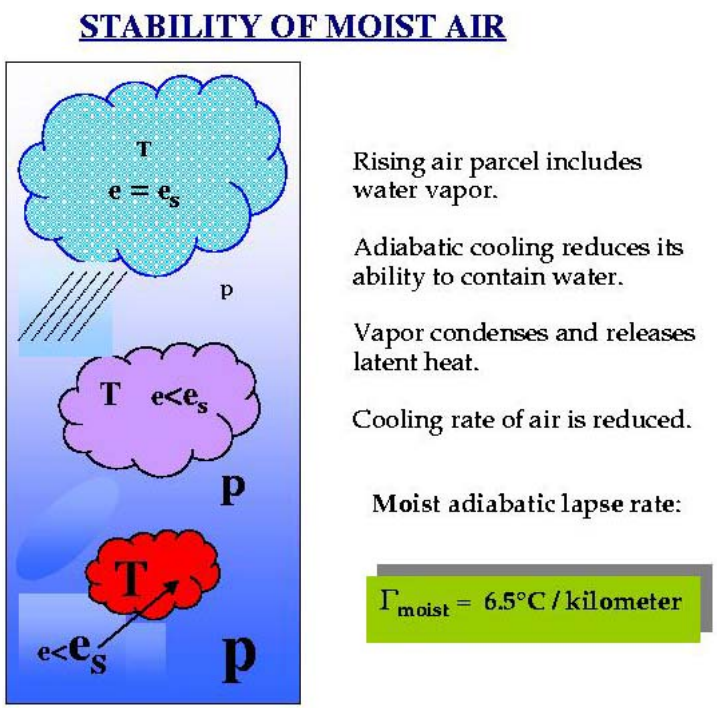


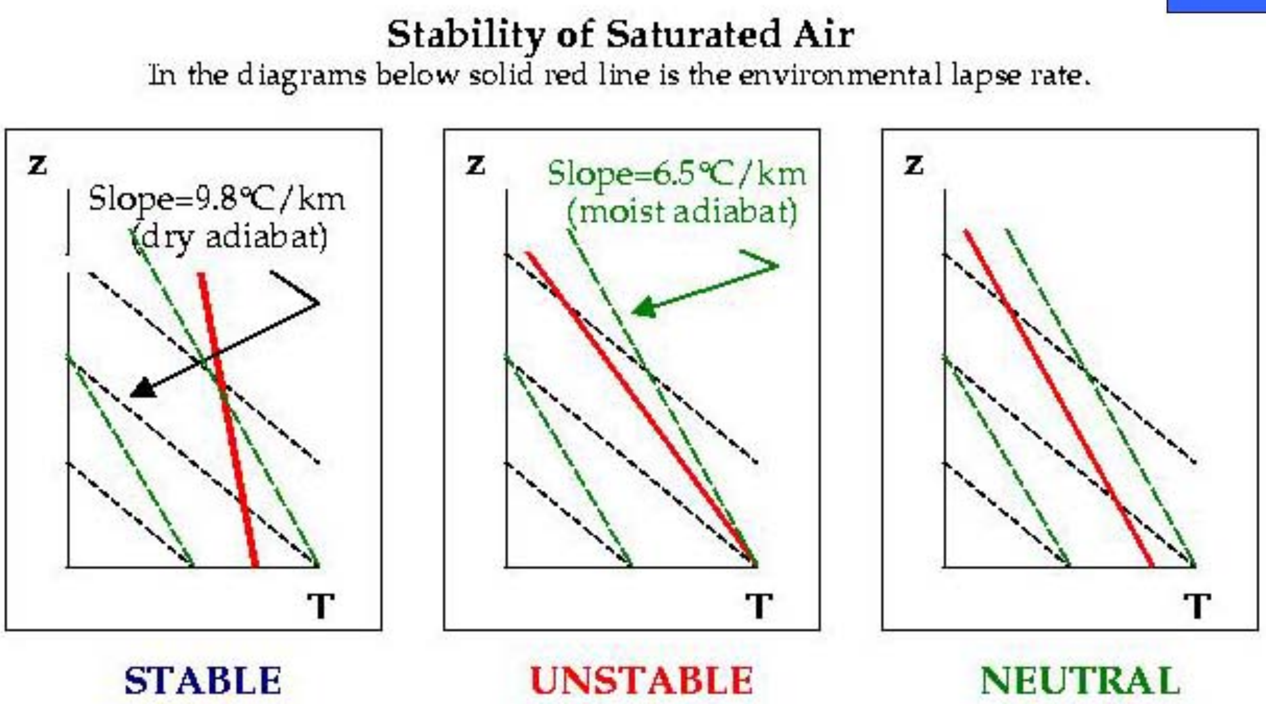


Atmospheric stability is assessed by comparing the environmental lapse rate with the adiabatic lapse rate

Atmospheric stability

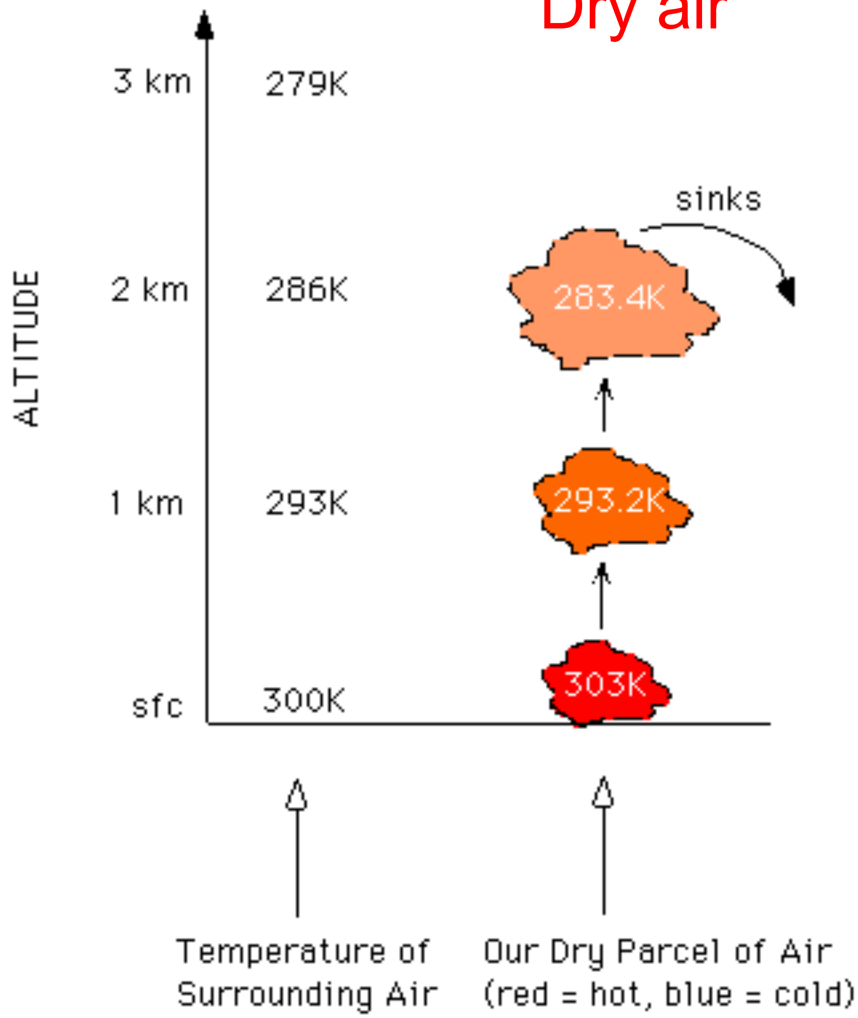
Moist air – condensation provides heat
Moist adiabatic lapse rate = ~6.5°C km^{-1}



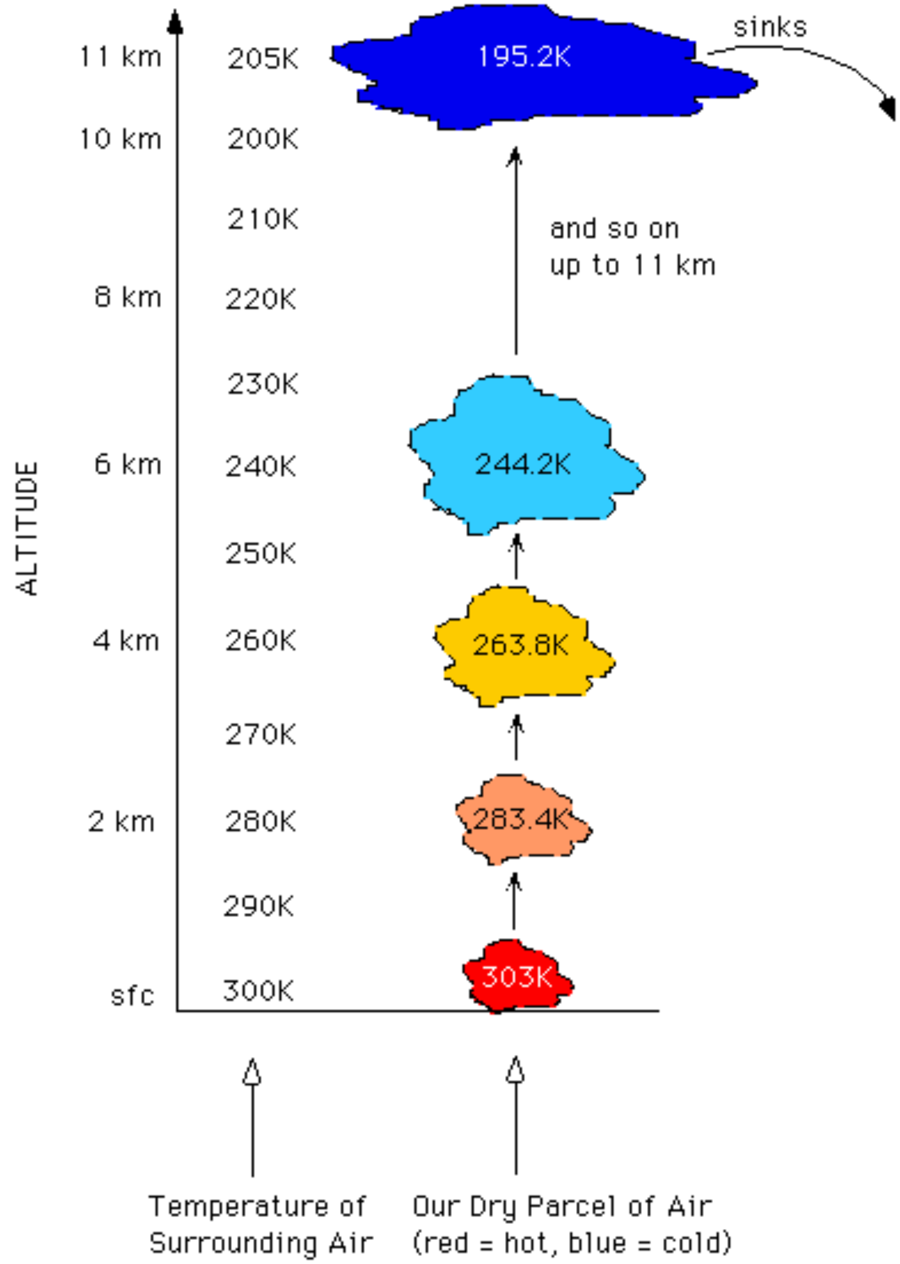


Atmospheric stability

Dry air

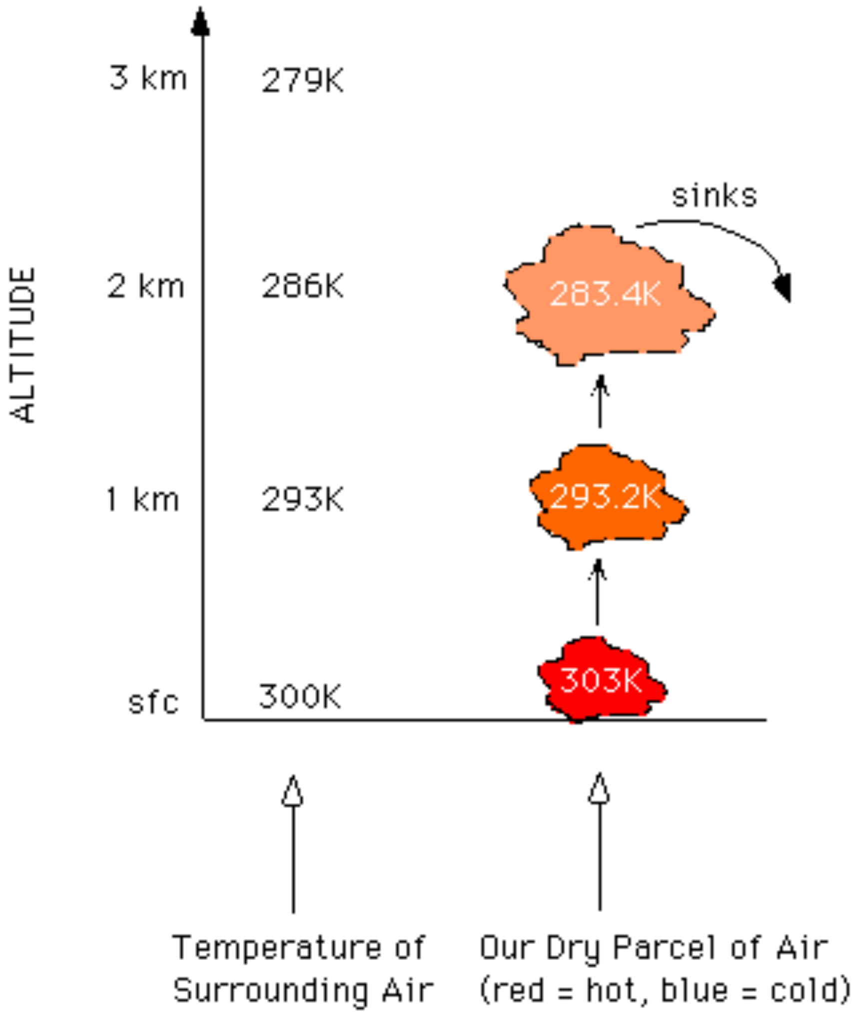


Lapse rate < adiabatic lapse rate

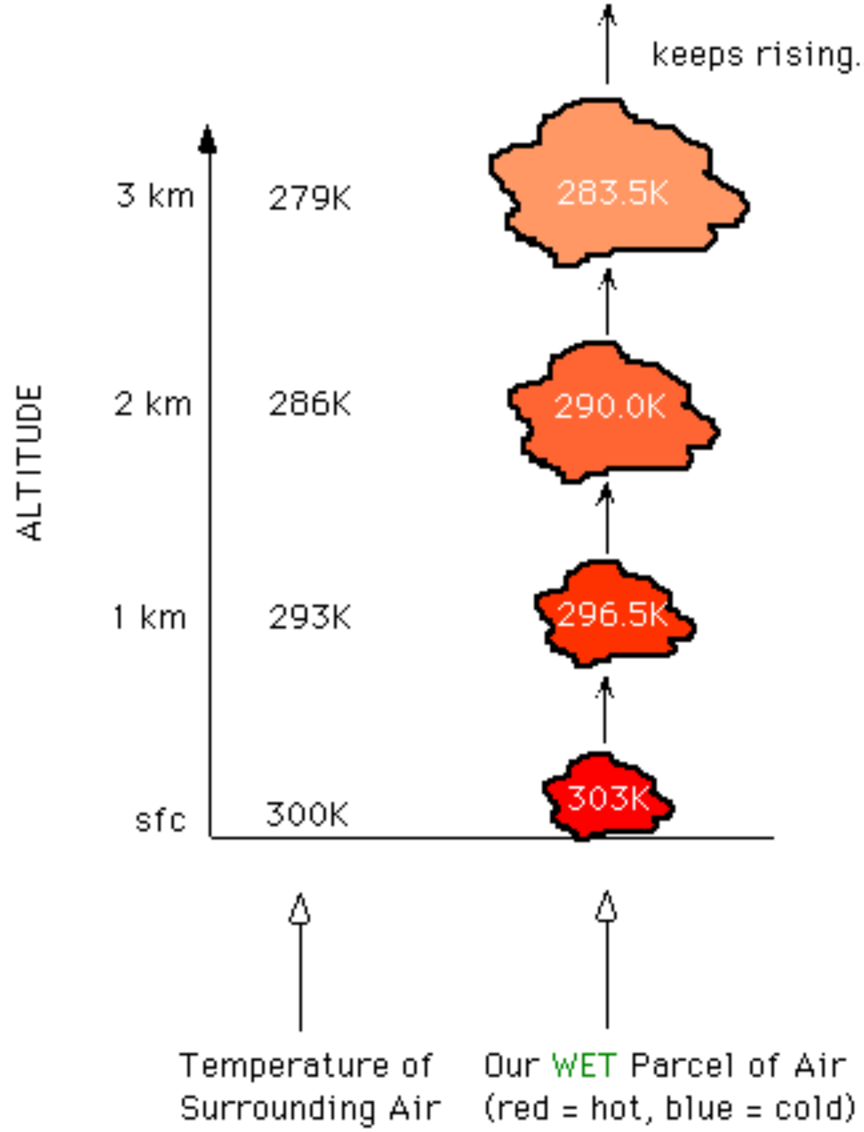


Lapse rate > adiabatic lapse rate

Atmospheric stability

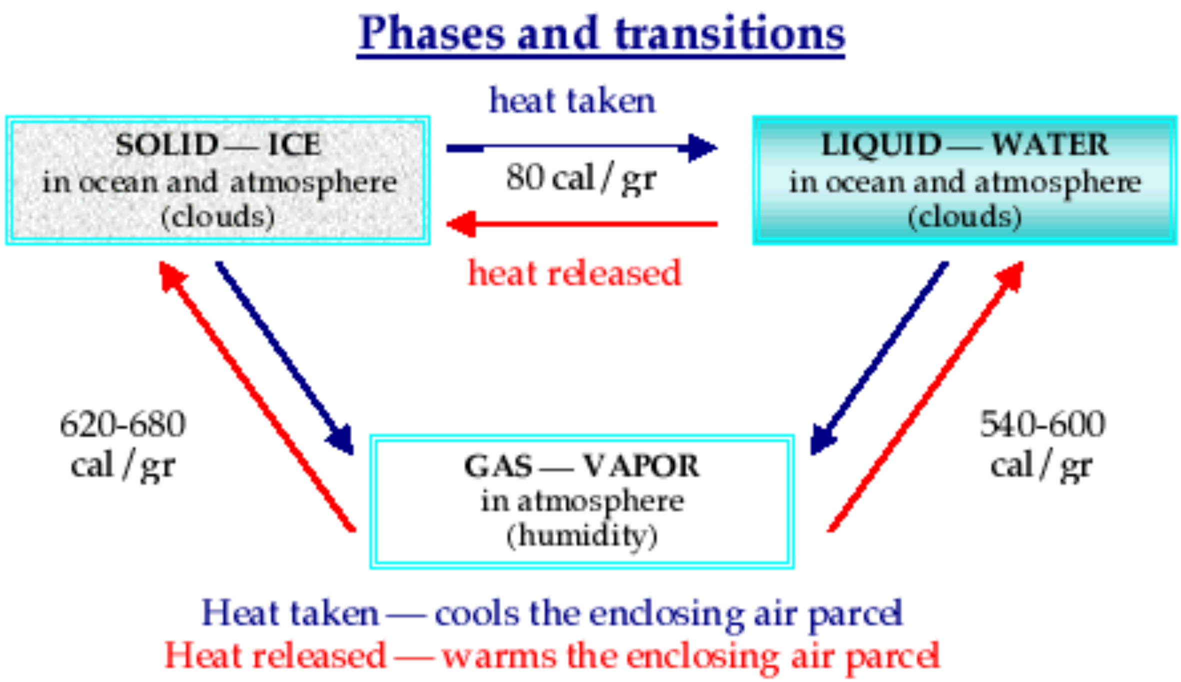


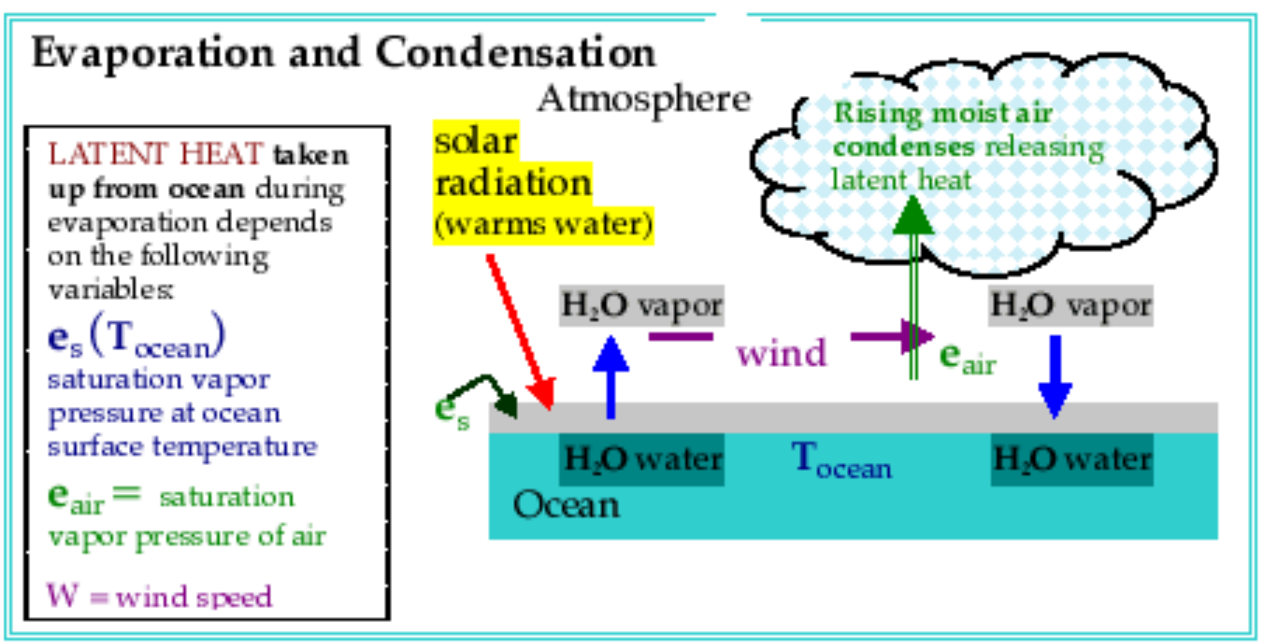
Lapse rate < dry adiabatic lapse rate



Same lapse rate > moist adiabatic lapse rate (Thunderstorm)

Water in the atmosphere





- There are about 13 million million tons of water vapor in the atmosphere (~0.33% by weight)
- In gas phase – absorbs longwave radiation and stores latent heat
- Responsible for ~70% of atmospheric absorption of radiation
- In liquid and solid phase – reflects and absorbs solar radiation

Temperature inversions

A temperature inversion occurs when a layer of cool air is trapped at ground level by an overlying layer of warm air, which can also trap pollutants. Many factors can lead to an inversion layer, such as temperatures that remain below freezing during the day, nighttime temperatures in the low teens to single digits, clear skies at night, and low wind levels.

Pollution trapping

Salt Lake valley, Utah

Radiosondes

• A radiosonde is a package of instruments mounted on a weather balloon that measures various atmospheric parameters and transmits the data to a fixed receiver (sometimes called a *rawinsonde* if wind speed is measured)

• Measured parameters usually include: pressure, altitude, latitude/longitude, temperature, relative humidity and wind speed/ direction

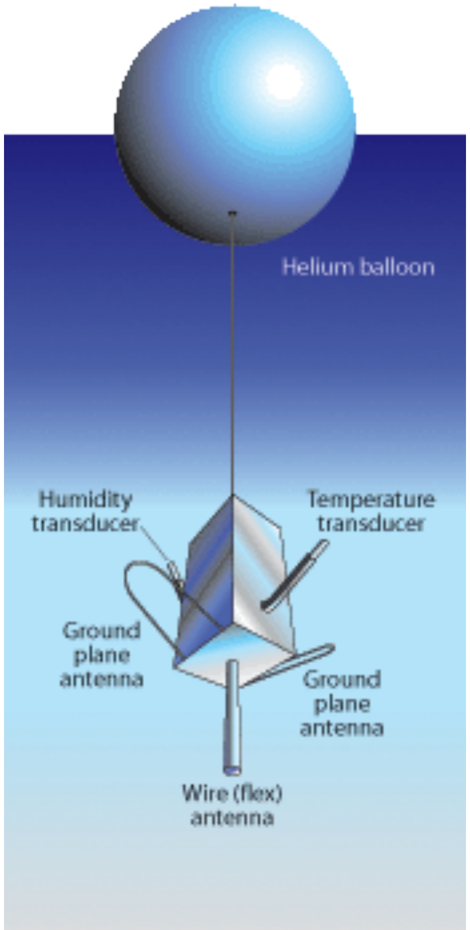
• The maximum altitude to which the helium or hydrogen-filled balloon ascends is determined by the diameter and thickness of the balloon

• At some pressure, the balloon expands to the extent that it bursts (maybe ~20 km) – the instrument is usually not recovered

• Worldwide there are more than 800 radiosonde launch sites

• Radiosonde launches usually occur at 0000 and 1200 UTC

• 'Snapshot' of the atmosphere for modeling and forecasting



Radiosonde soundings

• INFORMATION OBTAINED FROM RAOB SOUNDINGS:

• The radiosonde transmits temperature and relative humidity data at each pressure level. Winds aloft are determined from the precision radar tracking of the instrument package. The altitudes of these levels are calculated using an equation (*the hypsometric equation*) that relates the vertical height of a layer to the mean layer temperature, the humidity of the layer and the air pressure at top and bottom of the layer. Significant levels where the vertical profiles of the temperature or the dew point undergo a change are determined from the sounding. The height of the troposphere and stability indices are calculated.

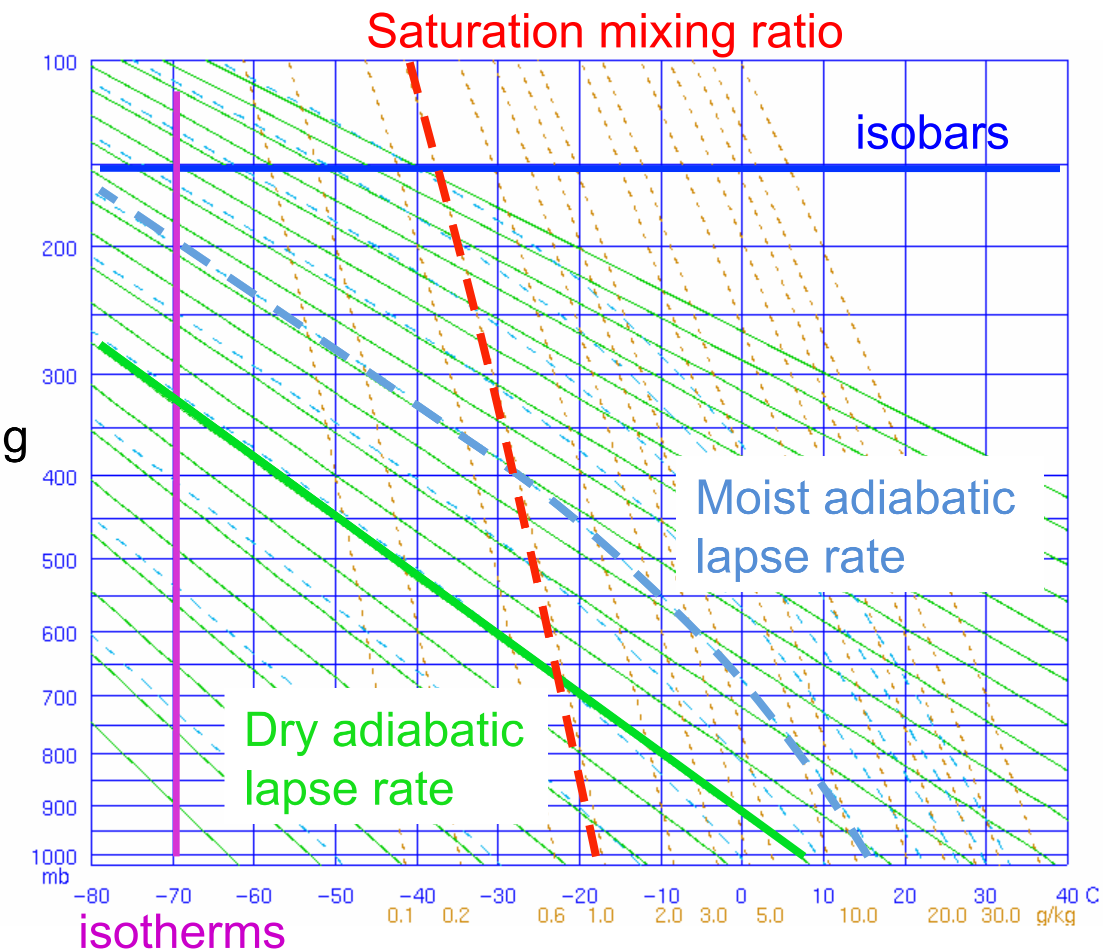
• A plot of the vertical variations of observed weather elements made above a station is called a sounding.

• The plots of the air temperature, dew point and wind information as functions of pressure are generally made on a specially prepared thermodynamic diagram.

Stüve diagrams

• A Stüve diagram is one of four thermodynamic diagrams used in weather data analysis and forecasting

• Radiosonde temperature and dew point data may be plotted on these diagrams to assess convective stability. Wind barbs may be plotted next to the diagram to indicate the vertical wind profile.



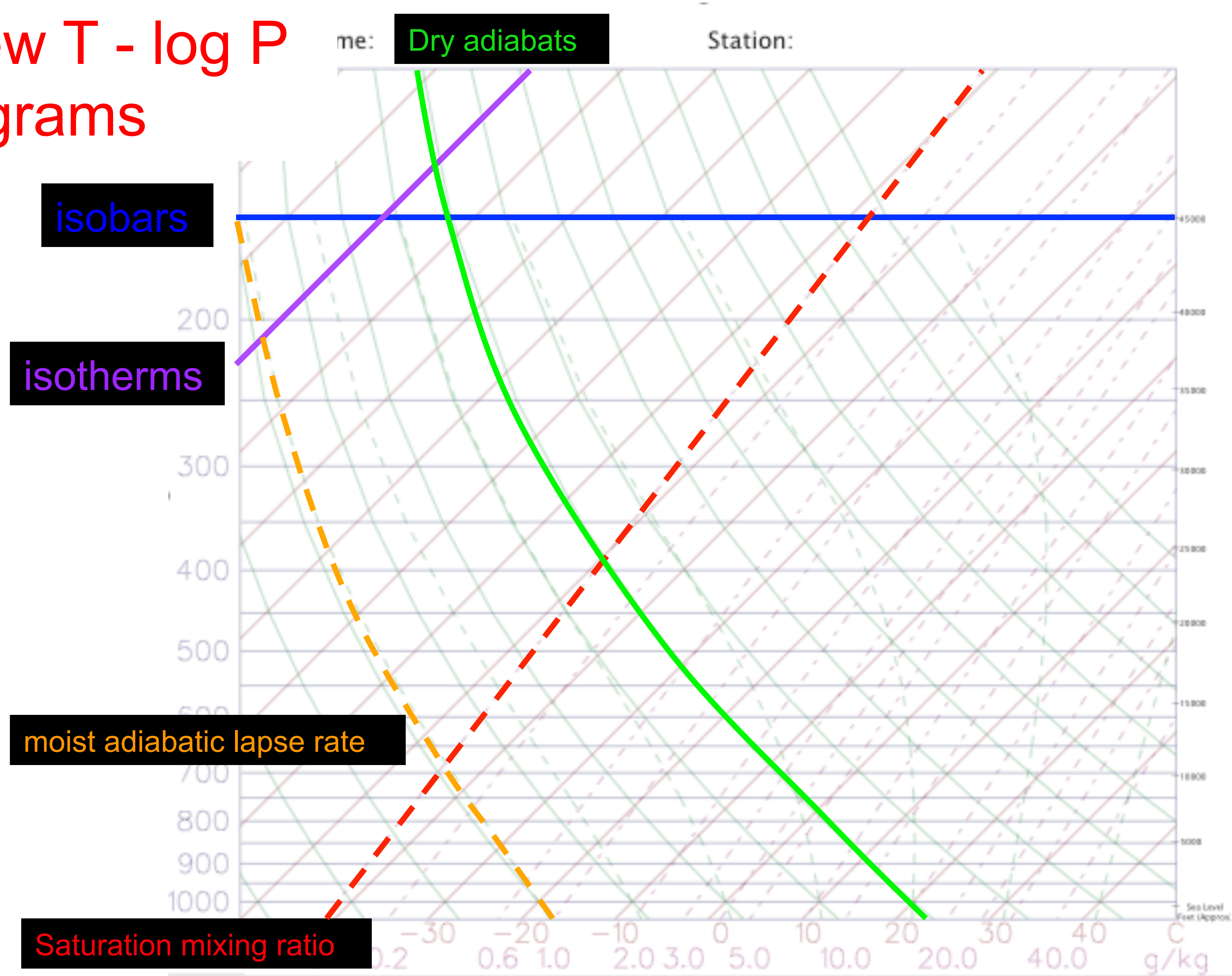
• Straight lines show the 3 primary variables: pressure, temperature and potential temperature

• Isotherms are straight and vertical, isobars are straight and horizontal

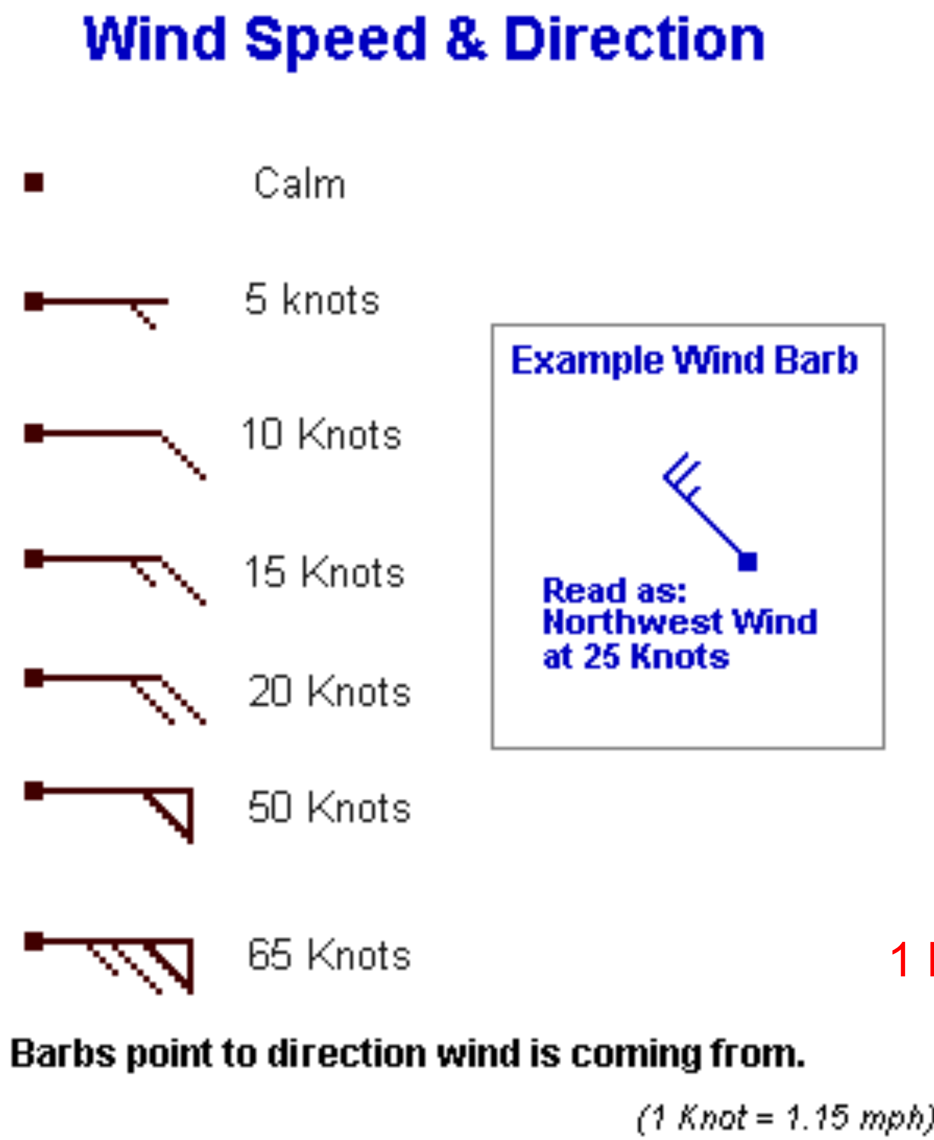
• Dry adiabats are straight and inclined 45º to the left; moist adiabats are curved

• Dew point: temperature to which air must be cooled (at constant pressure) for water vapor to condense to water (i.e. for clouds to form)

Skew T - log P diagrams



Wind barbs

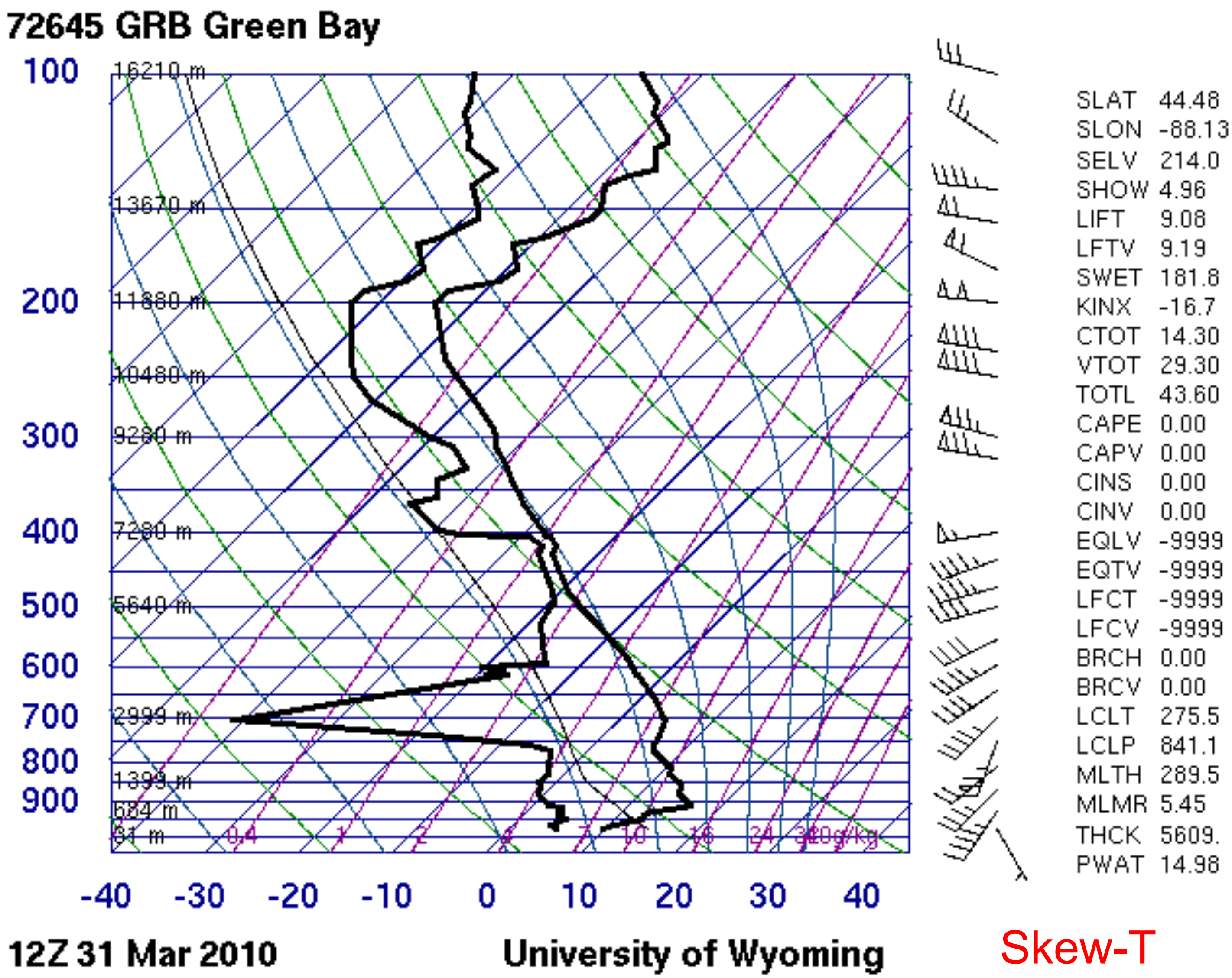


1 knot = 0.514 m s^{-1}

Radiosonde soundings

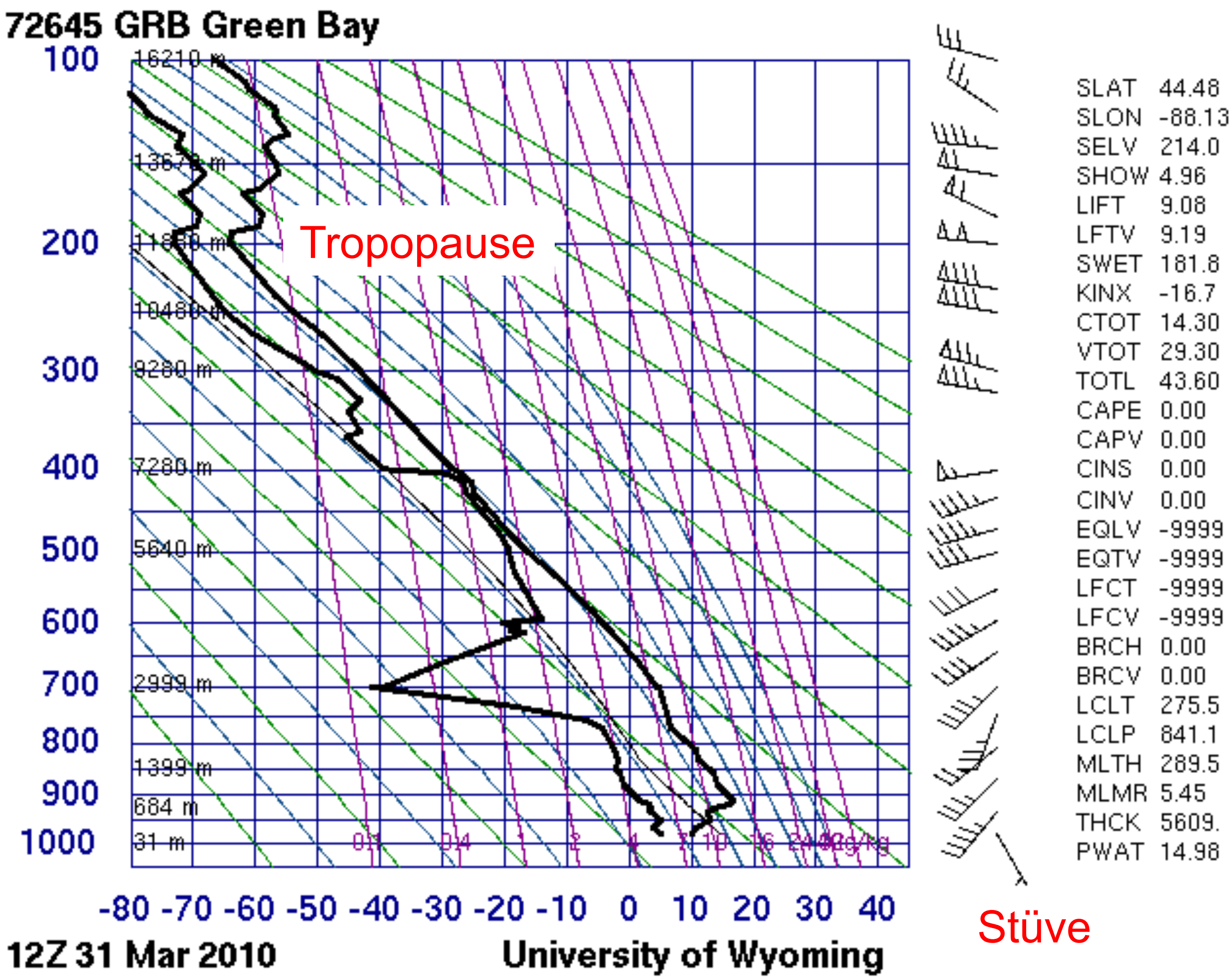
Currently, 70 RAOB stations are distributed across the continental USA
http://weather.uwyo.edu/upperair/sounding.html

Radiosonde sounding – Green Bay



Skew-T

Radiosonde sounding – Green Bay



Stüve

Ideal Gas Law

- The equation of state of an ideal gas – most gases are assumed to be ideal

$$PV = nRT$$

$$PV = NkT \qquad k = \frac{R}{N_A}$$

- **P** = pressure (Pa), **V** = volume taken up by gas (m^3), **n** = number of moles, **R** = gas constant (8.314 J mol^{-1} K^{-1}), **T** = temperature (K)
- **k** = Boltzmann constant (1.38×10^{-23} J K^{-1}), **N** = number of molecules, $\mathbf{N_A}$ = Avogadro constant (6.022×10^{23} molecules mol^{-1})

- Neglects molecular size and intermolecular attractions
- States that volume changes are inversely related to pressure changes, and linearly related to temperature changes
- Decrease pressure at constant volume = temperature must decrease (adiabatic cooling)

Values of the Universal Gas Constant R

$$\begin{aligned}
R &= 0.08205\ (l \cdot atm)/(mole \cdot K) \\
&= 8.205 \times 10^{-5}\ (m^3 \cdot atm)/(mole \cdot K) \\
&= 82.05\ (cm^3 \cdot atm)/(mole \cdot K) \\
&= 1.99 \times 10^{-3} kcal/(mole \cdot K) \\
&= 8.314\ (J)/(mole \cdot K) \\
&= 1.987\ (cal)/(mole \cdot K) \\
&= 62{,}358\ (cm^3 \cdot torr)/(mole \cdot K) \\
&= 62{,}358\ (cm^3 \cdot mm\ Hg)/(mole \cdot K)
\end{aligned}$$

Ideal gases

- Standard temperature and pressure (STP): varies with organization
- Usually $P = 101.325$ kPa (1 atm) and $T = 273.15$ K (0ºC)
- Sometimes $P = 101.325$ kPa and $T = 293.15$ K (20ºC)

- At STP (101.325 kPa, 273.15 K) each cm^3 of an ideal gas (e.g., air) contains 2.69×10^{19} molecules (or 2.69×10^{25} m^{-3})
- This number is the Loschmidt constant and can be derived by rearranging the ideal gas law equation:

$$N = \frac{PV}{kT}$$

- At higher altitudes, pressure is lower and the number density of molecules is lower

- Mean molar mass of air = 0.02897 kg mol^{-1} (air is mostly N_2)

Quantification of gas abundances

- The concentration (c) of a gas is the amount of gas in a volume of air:

$$c = \frac{Amount\ of\ gas}{Volume\ of\ air}$$

- 'Amount' could be mass, number of molecules, or number of moles
- Common units are *micrograms per m*^{3} (μg m^{-3}) or *molecules per m*^{3} – the latter is the number density of the gas. Partial pressures of gases are also sometimes used.
- We also define the mixing ratio of a gas:

$$x = \frac{Amount\ of\ gas}{Amount\ of\ air + gas}$$

- 'Amount' could be volume, mass, number of molecules, or number of moles. In atmospheric chemistry, it is usually volume.
- Example of a mixing ratio in *parts per million by volume* (ppmv; sometimes just written as ppm):

$$x_v = \frac{Unit\ volume\ of\ gas}{10^6\ unit\ volumes\ of\ (air + gas)}\ ppmv$$

Quantification of gas abundances

• Smaller mixing ratios are given in parts per billion (ppbv) or parts per trillion (pptv):

$$x_v = \frac{Unit\ volume\ of\ \ gas}{10^9\ \ unit\ volumes\ of\ \ (air + gas)}\ ppbv$$

$$x_v = \frac{Unit\ volume\ of\ \ gas}{10^{12}\ \ unit\ volumes\ of\ \ (air + gas)}\ pptv$$

• Mixing ratios can also be expressed by mass; the default is usually volume (i.e. ppb usually implies ppbv)

• For an ideal gas the volume mixing ratio is equal to the molar mixing ratio (x_m) or mole fraction (this is the SI unit for mixing ratios):

$$x_m = \frac{Moles\ of\ \ gas}{Moles\ of\ \ (air + gas)}$$

• So micromole per mole, nanomole per mole and picomole per mole are equivalent to ppmv, ppbv and pptv, respectively

• Remember the conversion factor! (ppmv = 10^6, ppbv = 10^9, pptv = 10^{12} etc.)

• MIXING RATIOS ARE INDEPENDENT OF TEMPERATURE AND PRESSURE

• Concentrations, however, are not (they change when air is transported)

Vertical profile of ozone

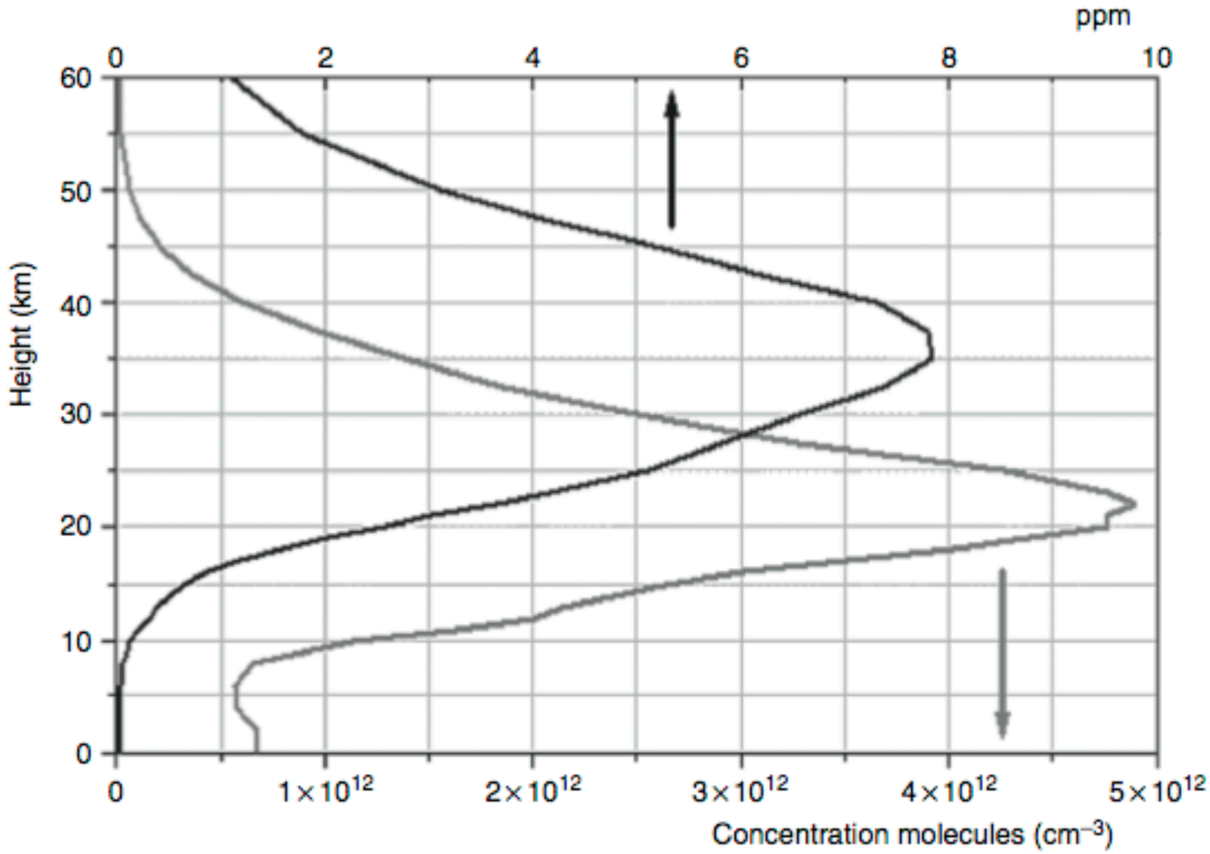


Fig. 2.2. Vertical profile of ozone in troposphere and stratosphere (US Standard Atmosphere), both in mixing ratio (in ppm or µmole per mole), peaking at about 36 km and concentration (molecules per cm^3), peaking at about 22 km

Vertical profiles of atmospheric constituents look different depending on the abundance units used

Conversion of abundance units

• For a gas *i,* the conversion between *number density* c_n (in molecules cm^{-3}) and *mass concentration* c_m (in grams cm^{-3}) is:

$$(c_m)_i = \frac{c_n M_i}{N_A}$$

• M_i = molecular weight of species *i* (grams mol^{-1})

• N_A = Avogadro constant (6.022×10^{23} molecules mol^{-1})

• Hence this conversion depends on the molecular mass of the gas

• Conversion from *number density* c_n (in molecules cm^{-3}) to volume mixing ratio:

$$x_v = c_n \frac{V}{N_A} \; or \; c_n = x_v \frac{N_A}{V}$$

• V = molar volume (cm^3) for the pressure and temperature at which the number density was measured

• At STP, V = 22414 cm^3 mole^{-1}. For arbitrary T and P, use the ideal gas law:

$$x_v = c_n \frac{RT}{PN_A} = c_m \frac{RT}{PM_i}$$

Abundance units for trace gases

Table 2.2. The different units for the abundance of atmospheric trace gases ($T = 293.15$K, $p = 101325$ Pa)

Trace gas	Molecular mass g/mole	Mixing ratio x_V ppb	Number density c_n molec. cm^{-3}	Concentration c_m µg m^3
O_3	48.00	1.000	$2.503 \cdot 10^{10}$	1.995
		0.501	$1.254 \cdot 10^{10}$	1.000
SO_2	64.06	1.000	$2.503 \cdot 10^{10}$	2.662
		0.376	$0.941 \cdot 10^{10}$	1.000
NO	30.01	1.000	$2.503 \cdot 10^{10}$	1.251
		0.799	$2.000 \cdot 10^{10}$	1.000
NO_2	46.01	1.000	$2.503 \cdot 10^{10}$	1.912
		0.532	$1.33 \cdot 10^{10}$	1.000
CH_4	16.04	1.000	$2.503 \cdot 10^{10}$	0.667
		1.500	$3.755 \cdot 10^{10}$	1.000
CH_2O	30.03	1.000	$2.503 \cdot 10^{10}$	1.248
		0.801	$2.005 \cdot 10^{10}$	1.000
CO	28.01	1.000	$2.503 \cdot 10^{10}$	1.164
		0.859	$2.150 \cdot 10^{10}$	1.000

Spectroscopic remote sensing techniques give results in number density, not mixing ratios (recall Beer's Law)

Unit conversion example

- The Hong Kong Air Quality Objective for ozone is 240 μg m^{-3}
- The U.S. National Ambient Air Quality Standard for ozone is 120 ppb
- Which standard is stricter at the same temperature (25ºC) and pressure (1 atm)?

$$x_v = c_m \frac{RT}{PM_i}$$

- REMEMBER TO USE CONSISTENT (SI) UNITS
- We need to convert 240 μg m^{-3} to a mixing ratio in ppb
- On the right hand side we have:

$$x_v = c_m \frac{8.314\, J\, K^{-1}\, mol^{-1} \times 298\, K}{101325\, Pa \times 48\, g\, mol^{-1}}$$

$$= c_m \frac{8.314\, J\, K^{-1}\, mol^{-1} \times 298\, K}{101325\, J\, m^{-3} \times 48\, g\, mol^{-1}}$$

- So we need c_m in g m^{-3}
- Which is 240×10^{-6} g m^{-3}
- This gives $x_v = 1.22\times10^{-7} \times 10^{9}$ nanomoles per mole = 122 ppb

Column density

- Another way of expressing the abundance of a gas is as column density (S_n), which is the integral of the number density along a path in the atmosphere

$$S_n = \int_{path} c_n(s)\, ds$$

- The unit of column density is molecules cm^{-2}
- The integral of the mass concentration is the mass column density S_m (typical units are µg cm^{-2})

$$S_m = \int_{path} c_m(s)\, ds$$

- Usually the path is the entire atmosphere from the surface to infinity, called the total column, giving the total (vertical) atmospheric column density, V:

$$V = \int_0^{\infty} c_n(z)\, dz$$

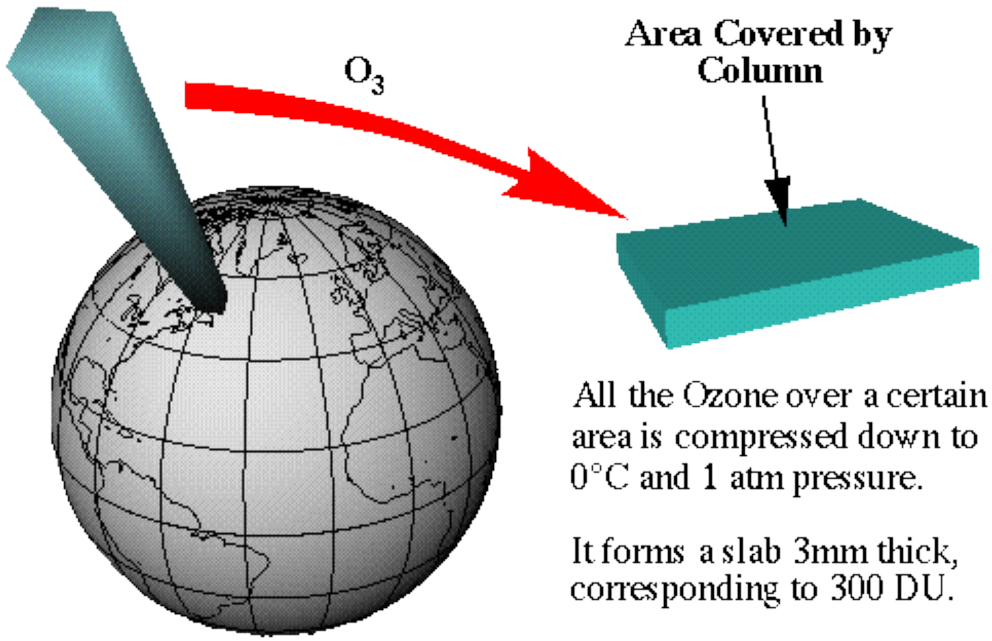
Dobson Units

• A Dobson Unit [DU] is a unit of column density used in ozone research, and in measurements of SO_2

• Named after G.M.B. Dobson, one of the first scientists to investigate atmospheric ozone (~1920 – 1960)

• The illustration shows a column of air over Labrador, Canada. The total amount of ozone in this column can be conveniently expressed in Dobson Units (as opposed to typical column density units).

• If all the ozone in this column were to be compressed to STP (0ºC, 1 atm) and spread out evenly over the area, it would form a slab ~3 mm thick



• 1 Dobson Unit (DU) is defined to be 0.01 mm thickness of gas at STP; the ozone layer represented above is then ~300 DU (NB. 1 DU also = 1 milli atm cm)

Dobson Units

• So 1 DU is defined as a 0.01 mm thickness of gas at STP

• We know that at STP (101.325 kPa, 273.15 K) each cm^3 of an ideal gas (e.g., air, ozone, SO_2) contains 2.69×10^{19} molecules (or 2.69×10^{25} m^{-3})

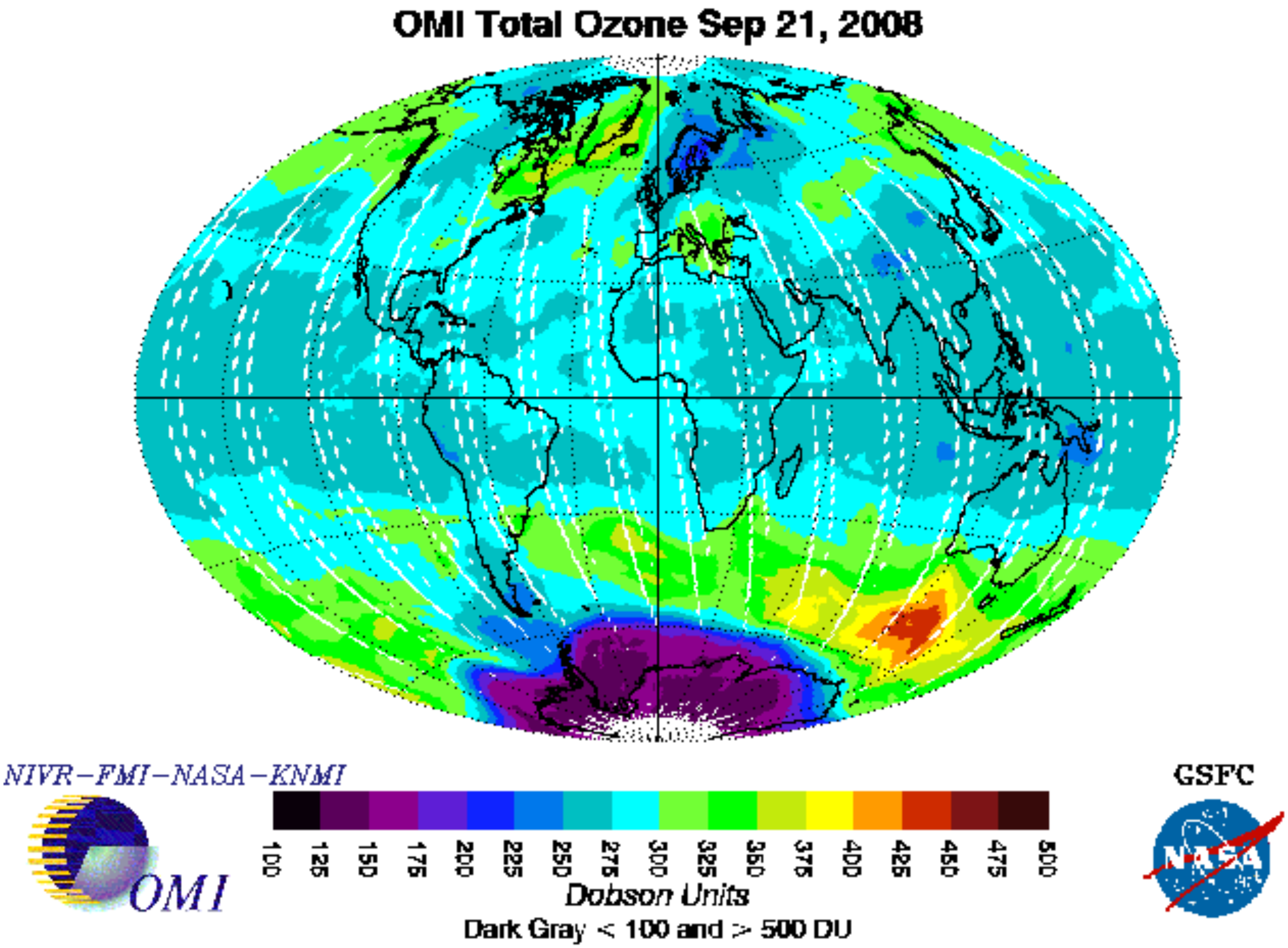
• So a 0.01 mm thickness of an ideal gas contains:

2.69×10^{19} molecules cm^{-3} × 0.001 cm = 2.69×10^{16} molecules cm^{-2} =1 DU

• Using this fact, we can convert column density in Dobson Units to mass of gas, using the cross-sectional area of the measured column at the surface

• For satellite measurements, the latter is represented by the 'footprint' of the satellite sensor on the Earth's surface

The Ozone Layer



- Map shows total column ozone in DU

Lifetimes of trace gases

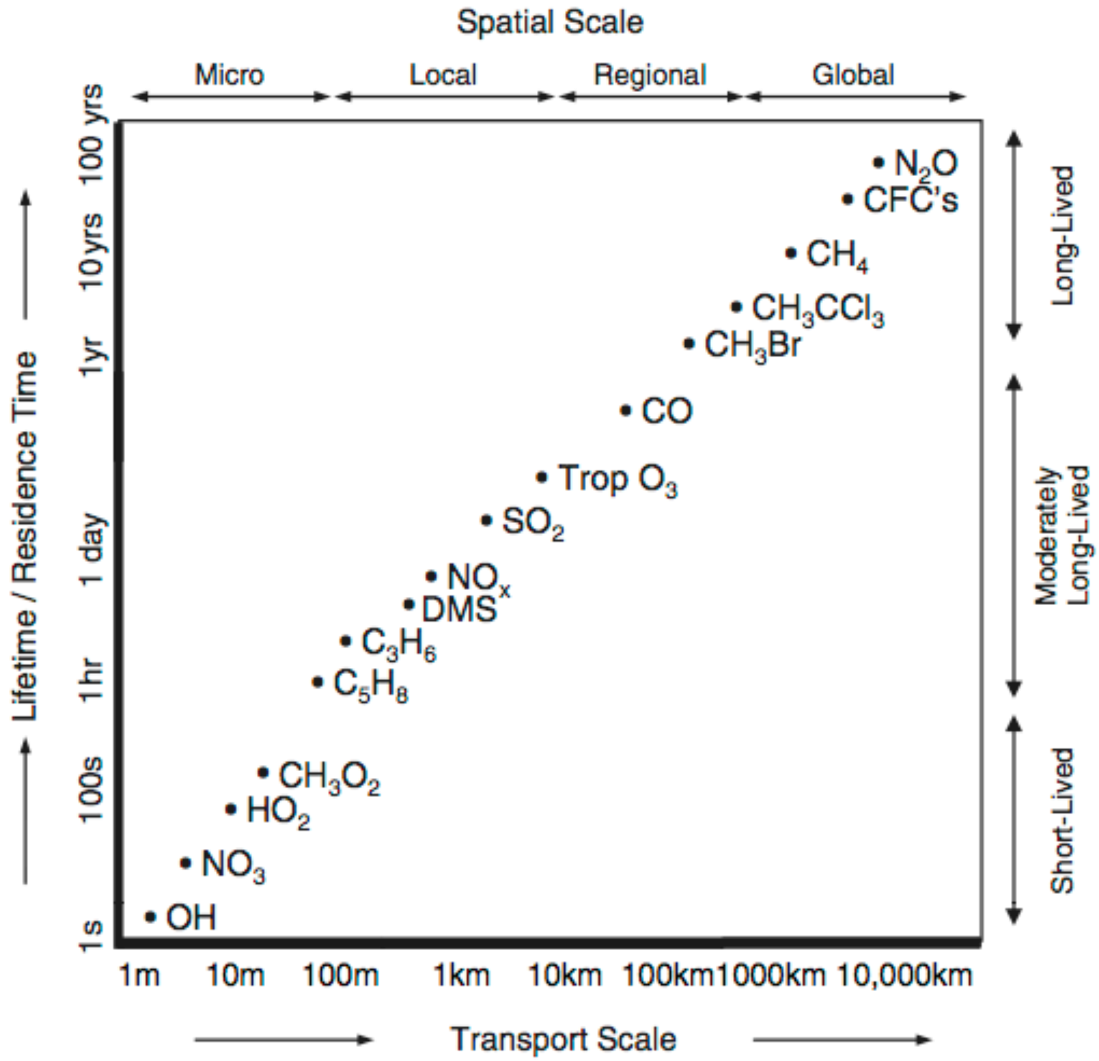


Fig. 2.3. Average lifetimes (residence times) of gases in the atmosphere range from seconds (and below) to millennia. Accordingly, transport can occur on scales reaching from a few meters to the global scale (adapted from Seinfeld and Pandis, 1998)