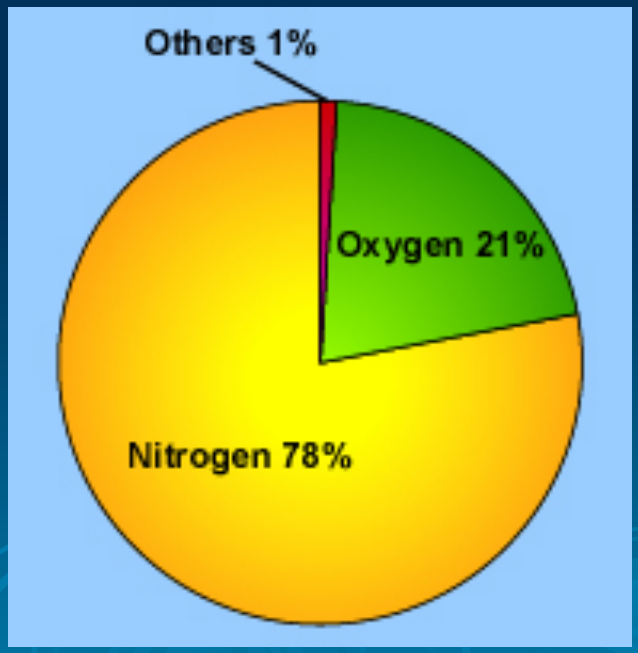
CLIM-319/GGS-319
Measures of Atmospheric Composition

- Atmospheric Composition
- Measures of Atmospheric Composition
  - Mixing Ratio
  - Number Density
  - Partial Pressure



Earth System

- ✓ Is there anything in this picture that is not influenced by water?
- ✓ Is there anything in this picture not influenced by life?
- ✓ Is there anything in this picture not influenced by the atmosphere?



Characteristics of Earth System

- Cyclical flow in a closed Earth system

- In this closed system Lithosphere (Earth's crust), Hydrosphere (oceans, lakes, rivers, ground water), Atmosphere, and Biosphere (vegetation & animals) are interacting



Atmospheric Composition

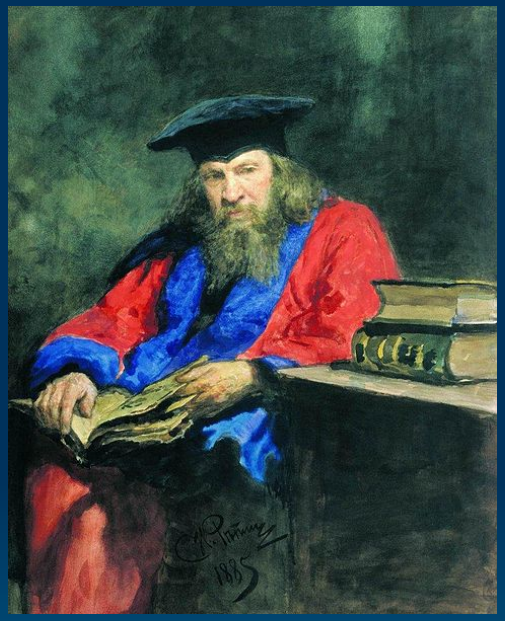
- From an Earth system perspective
  - The composition of the atmosphere is controlled by the exchange of elements between the different reservoirs ("spheres") of the Earth such as
  - Reservoirs on Earth
    - Atmosphere (gases, water vapor)
    - Biosphere (vegetation, animals)
    - Hydrosphere (oceans, lakes, rivers, ground water)
    - Lithosphere (Earth's crust)

Earth System Cycles (Natural Elements)

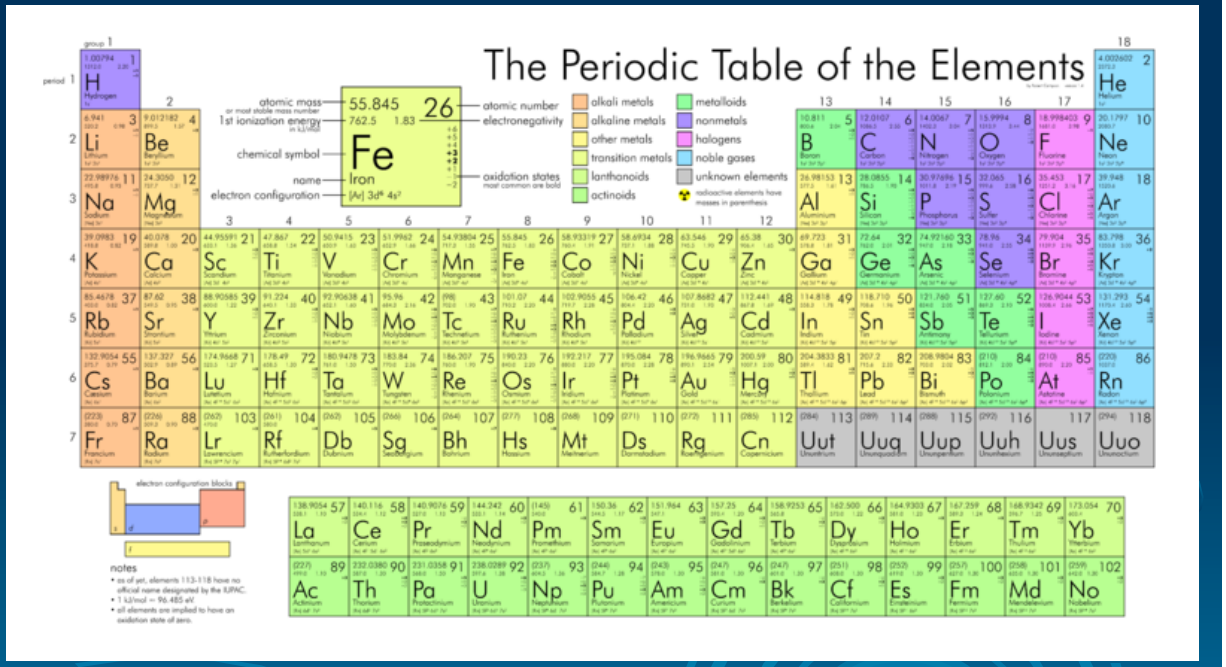
- Natural elements
  - There are 92 natural elements
  - About 25 of the 92 natural elements are known to be essential to life
    - Approximately 96% of living material are made from
      - Carbon (C) 18.5 %
      - Hydrogen (H) 9.5%
      - Nitrogen (N) 3.3%
      - Oxygen (O) 65%
    - Approximately 4% of living material are made from
      - Calcium (Ca) 1.5%
      - Phosphorus (P) 1.0%
      - Potassium (K) 0.4%
      - Sulfur (S) 0.3%
      - Sodium (Na) 0.2
      - Chlorine (Cl) 0.2%
      - Magnesium (Mg) 0.1%

Earth System Cycles (Chemical Elements)

- A chemical element is a pure chemical substance consisting of one type of atom distinguished by its atomic number which is the number of protons in its nucleus



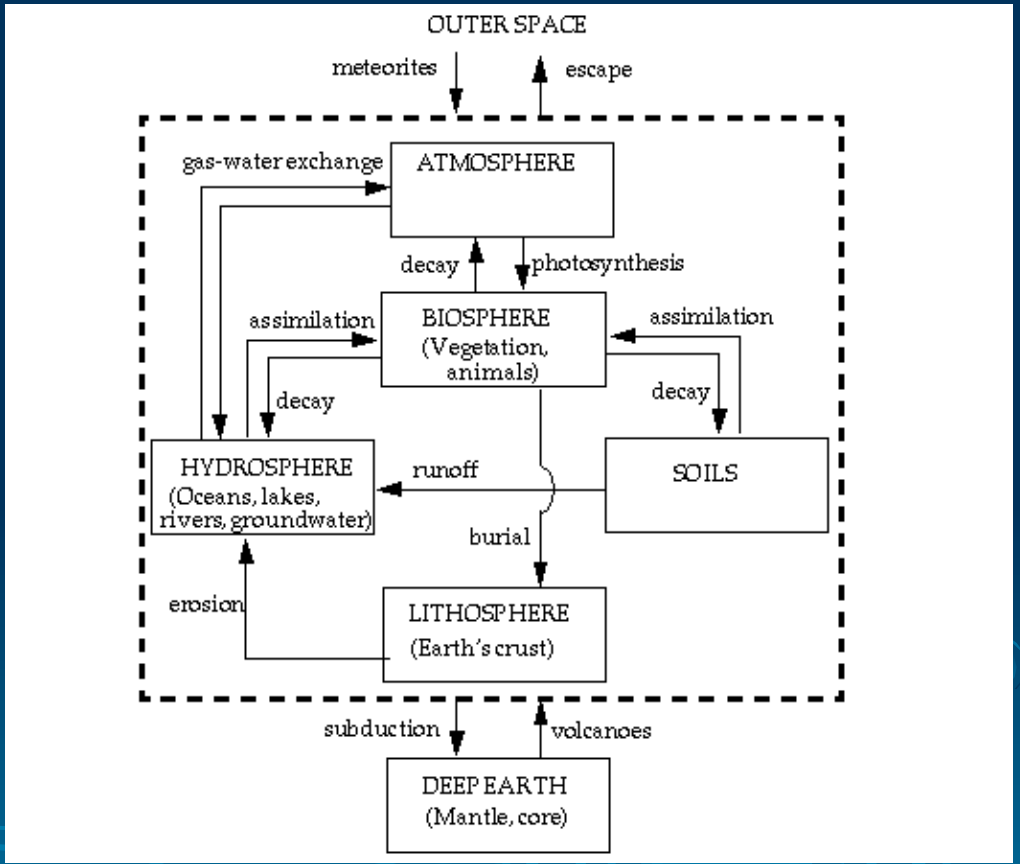
Russian chemistry professor Dmitri Mendeleev published the first periodic table in 1869



Earth System Cycles

- The Earth system is an assemblage of atoms of the 92 natural elements
- Almost all of these atoms have been present in the Earth system since the formation of the Earth 4.5 billion years ago by gravitational accretion of a cloud of gases and dust
- Extraterrestrial sources (meteors) are relatively unimportant
- Escape of atoms to outer space is prevented by gravity except for the lightest atoms (Hydrogen & Helium)

The Earth System mass is conserved!



Early Evolution of The Atmosphere

- Supply of elements to the surface reservoirs was set in the earliest stages of Earth's history when the crust formed and volcanic outgassing transferred material from the deep Earth to the atmosphere
- Early atmosphere = Volcanic gases
  - It was mostly H_2O (~95%), CO_2, N_2, and sulfur gases (No free O_2)
- The outgassed water precipitated to form oceans
- CO_2, and sulfur gases then dissolved in the oceans, leaving N_2 as the dominant gas in the atmosphere

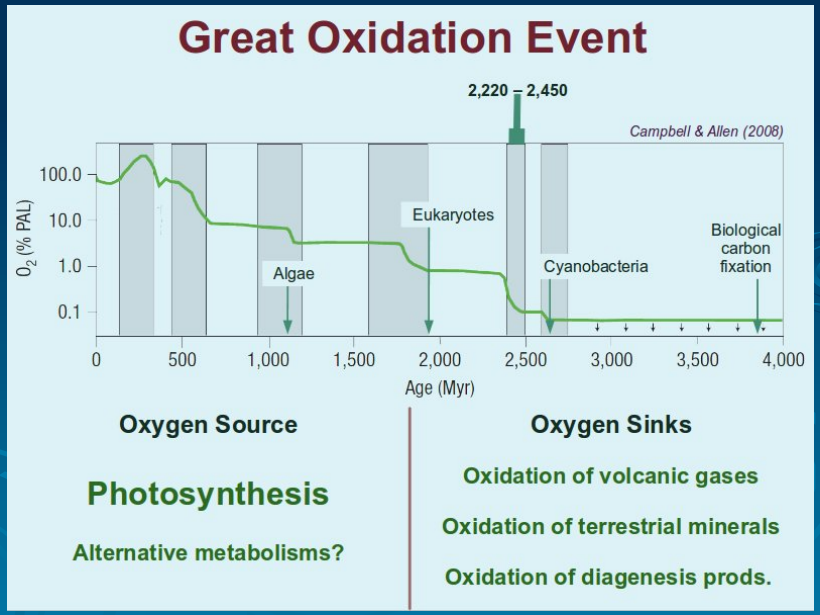




Early Evolution of The Atmosphere

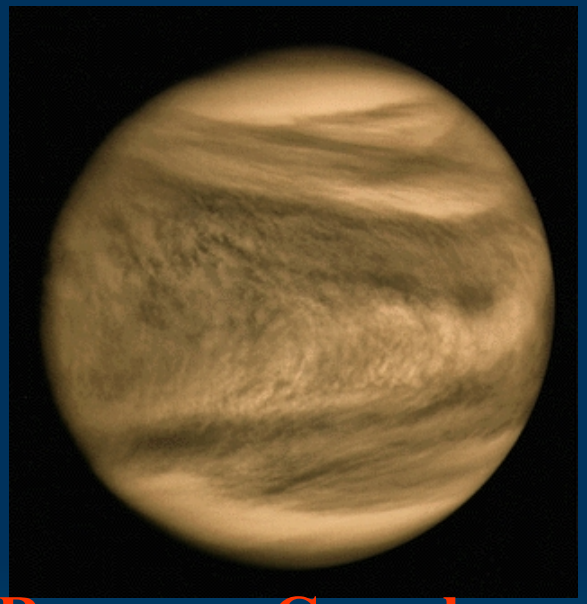
- The presence of liquid water allowed the development of living organisms.
- About 3.5 billion years ago, some organisms developed the capacity to convert CO_2 to organic carbon by photosynthesis
- This process released O_2 which gradually accumulated in the atmosphere, reaching its current atmospheric concentration about 400 million years ago





Early Evolution of The Atmosphere

Venus



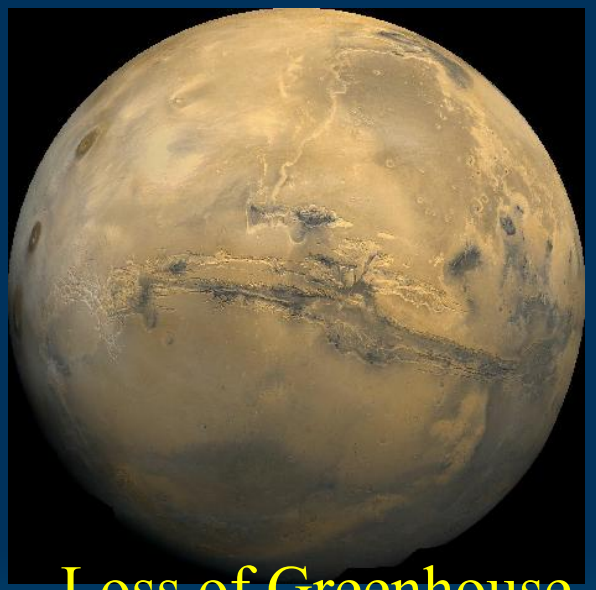
Runaway Greenhouse

Earth



Robust Biosphere

Mars

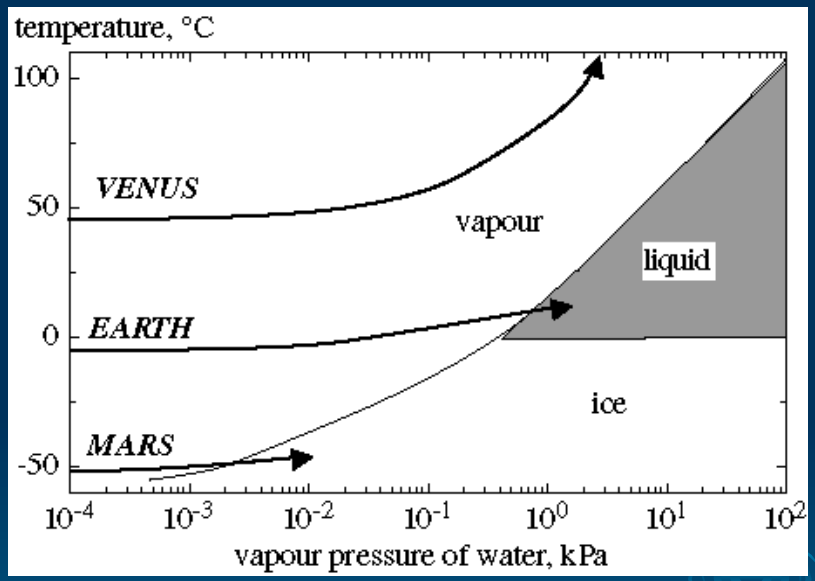


Loss of Greenhouse gases CO_2 & H_2O

- It is instructive to compare the evolution of the Earth's atmosphere to that of its neighbor planes Venus and Mars
- All three planets presumably formed with similar assemblages of elements but their present-day atmospheric compositions are vastly different

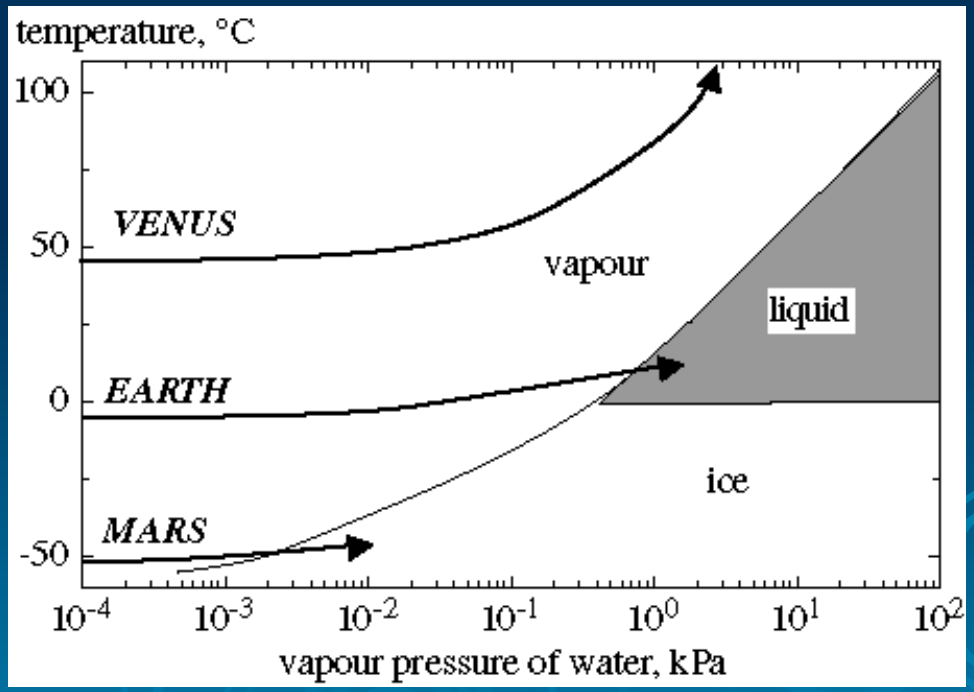
Early Evolution of The Atmosphere

- Venus has an atmosphere ~100 times thicker than that of Earth and consisting mostly CO_2
- Because of the greater proximity of Venus to the Sun, the temperature of the early Venus was too high for the outgassed water to condense and form oceans
- Water vapor in Venus's upper atmosphere photolyzed to produce H atoms that escaped the planet's gravitational field and the O atoms left behind were removed by oxidation of rocks
- This mechanism is thought to explain the low H_2O concentration in the Venusian atmosphere



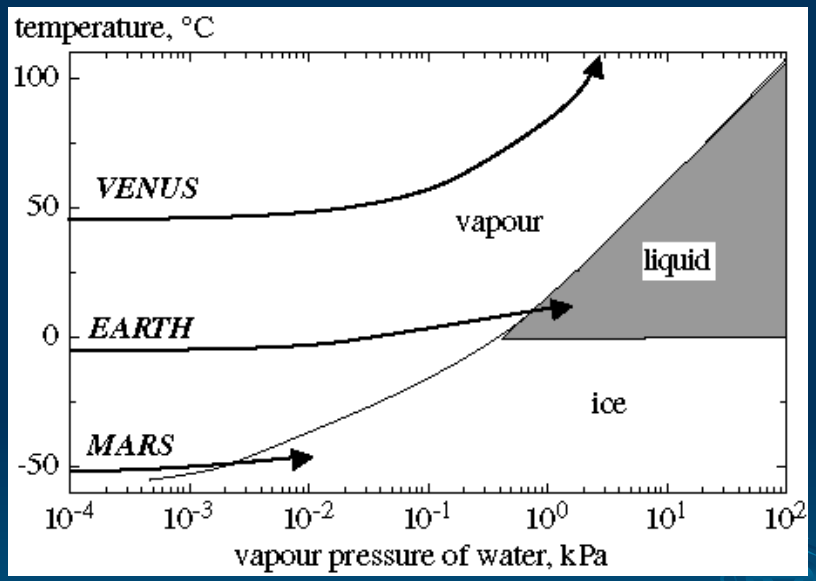
Early Evolution of The Atmosphere

- On Earth, by contrast, the atmosphere contains only 10^{-5} of all water in the surface reservoirs (the bulk is in the oceans) so that loss of water to outer space is extremely slow and is compensated by evaporation from the oceans



Early Evolution of The Atmosphere

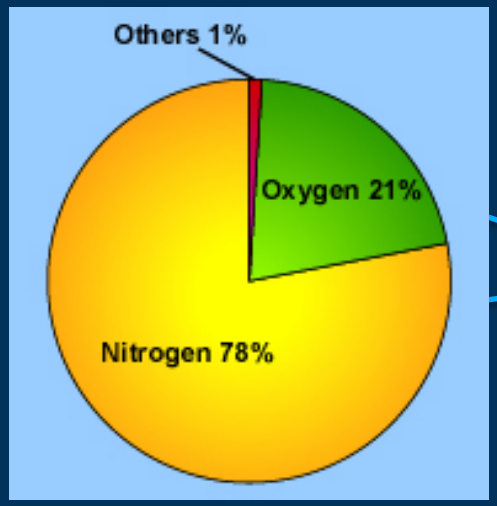
- The atmosphere of Mars is much thinner than that of the Earth and consists principally of CO_2
- The smaller size and hence weaker gravitational field of Mars allows easier escape of H atoms to outer space
- Although the mixing ratio of CO_2 in the Martian atmosphere is high, its total abundance is in fact extremely low compared to that of Venus
- It is thought that CO_2 has been removed from the Martian atmosphere by surface reactions producing carbonate rocks



Early Evolution of The Atmosphere

	Venus	Earth	Mars
Radius (km)	6100	6400	3400
Mass of planet (1023 kg)	49	60	6.4
Gravity (m s^{-2})	8.9	9.8	3.7
Surface temperature (K)	730	290	220
Surface pressure (mb)	9100	1000	7
Atmospheric composition (mol/mol)			
CO_2	0.96	$4X10^{-4}$	0.95
N_2	$3.4X10^{-2}$	0.78	$2.7X10^{-2}$
O_2	$6.9X10^{-5}$	0.21	$1.3X10^{-3}$
H_2O	$3X10^{-3}$	$1X10^{-2}$	$3X10^{-4}$

Current Atmospheric Composition



- Gases at extremely low concentrations are called trace gases
- For their measures, ppm (parts per million volume) or ppb, ppt can be used.

Atmospheric Composition

Constituent[a]	Molecular weight	Fractional concentration by volume
Nitrogen (N_2)	28.013	78.08%
Oxygen (O_2)	32.000	20.95%
Argon (Ar)	39.95	0.93%
Water vapor (H_2O)	18.02	0–5%
Carbon dioxide (CO_2)	44.01	380 ppm
Neon (Ne)	20.18	18 ppm
Helium (He)	4.00	5 ppm
Methane (CH_4)	16.04	1.75 ppm
Krypton (Kr)	83.80	1 ppm
Hydrogen (H_2)	2.02	0.5 ppm
Nitrous oxide (N_2O)	56.03	0.3 ppm
Ozone (O_3)	48.00	0–0.1 ppm

[a] So called *greenhouse gases* are indicated by bold-faced type. For more detailed information on minor constituents, see Table 5.1.

Measures of Atmospheric Composition

- The objective of atmospheric chemistry is to understand the factors that control the concentration of chemical species in the atmosphere
- Three principal measures
  - Mixing ratio
  - Number density
  - Partial pressure

Mixing Ratio, C

Mixing ratio: The mixing ratio C_x of a gas X is defined as the number of moles of X per mole of air, or equivalently in units of volume of gas per volume of air

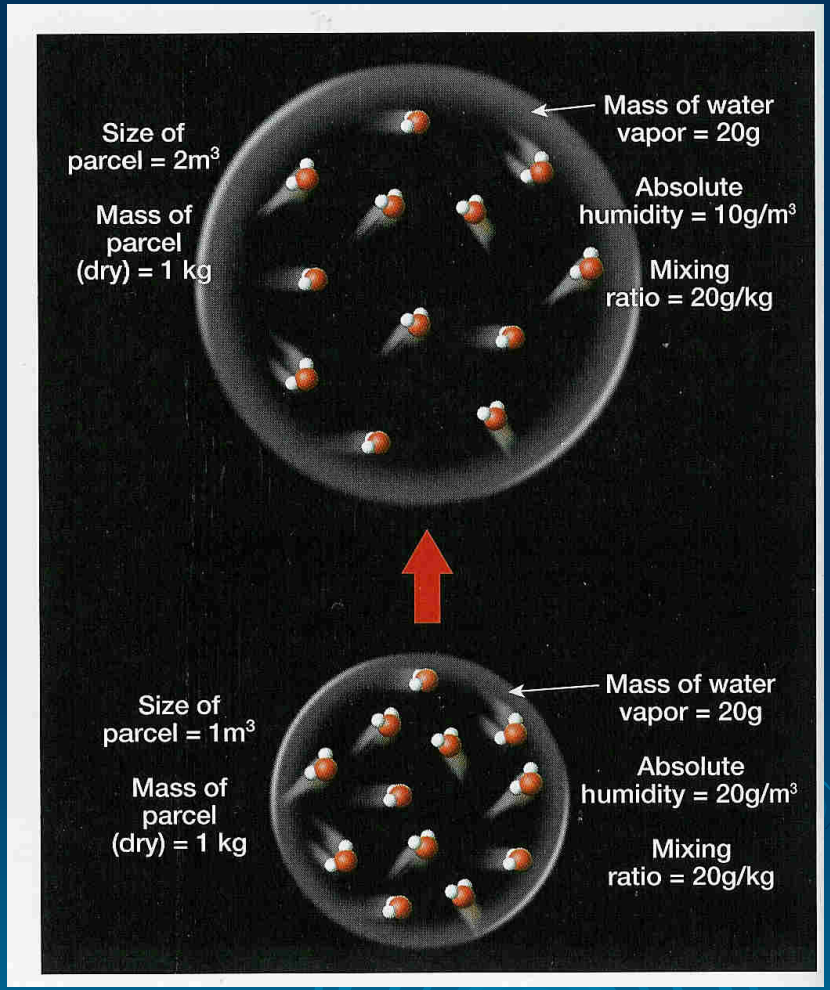
For example,

$$\text{Mixing ratio} = \frac{\text{mass of water vapor (grams)}}{\text{mass of dry air (kilograms)}}$$

Because it is measured in units of mass (usually gram per kilogram), the mixing ratio is unaffected by changes in volume or pressure.

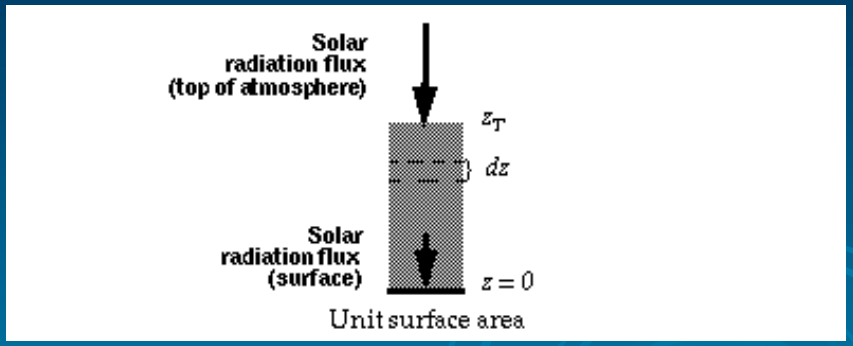
Mixing Ratio, C

- The mixing ratio of a gas has the virtue of remaining constant when the air density changes (as happens when the temperature or the pressure changes).
- Consider a balloon filled with room air and allowed to rise in the atmosphere. As the balloon rises it expands, so that the number of molecules per unit volume inside the balloon decreases; however, the mixing ratios of the different gases in the balloon remain constant.
- The mixing ratio is therefore a robust measure of atmospheric composition.



Number Density, n

- The number density n_x of a gas X is defined as the number of molecules of X per unit volume of air (e.g., molecules of air per cm^3)
- Number densities are critical for calculating gas-phase reaction rates.
- Another important application of number densities is to measure the absorption or scattering of a light beam by an optically active gas.
- The integral over the depth of the atmosphere defines the atmospheric column of X.
- This atmospheric column determines the total efficiency with which the gas absorbs or scatters light passing through the atmosphere
- For example, the efficiency with which the ozone layer prevents harmful solar UV radiation from reaching the Earth's surface is determined by the atmospheric column of ozone



$$Column = \int_0^{z_T} n_x \, dz$$

Ideal Gas Law

- The number density and the mixing ratio of a gas are related by the number density of air na (molecules of air per cm3 of air):

$$n_x = C_x n_a$$

- The number density of air is in turn related to the atmospheric pressure P by the ideal gas law.
- Consider a volume V of atmosphere at pressure P and temperature T containing N moles of air. The ideal gas law gives
- Note that the number density of air is related to N and V

$$PV = NRT$$

Ideal Gas Law

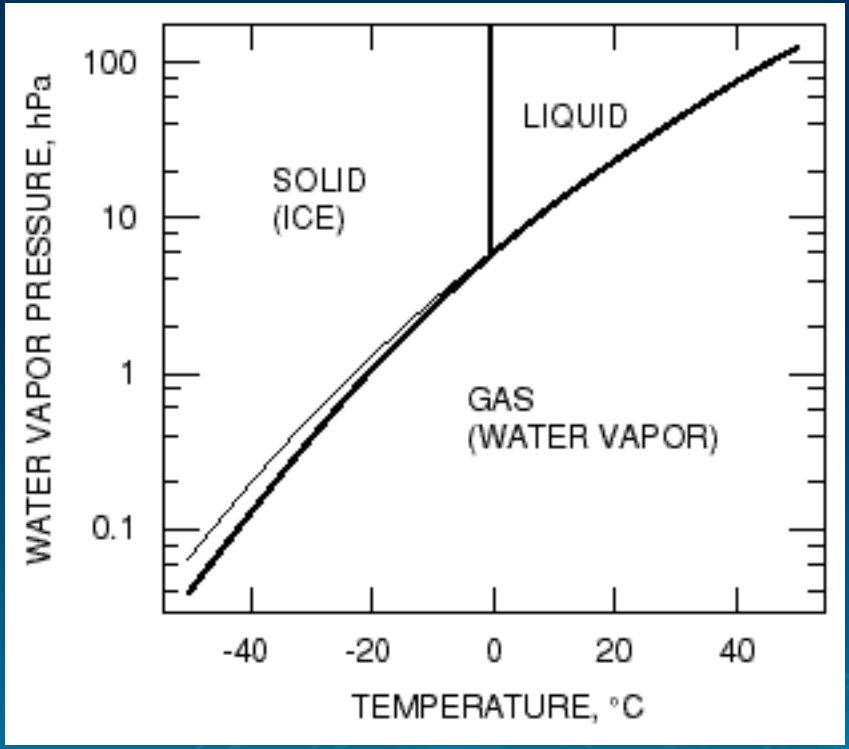
- Three state atmospheric variables (pressure (p), temperature (T), and density)
- The ideal gas law relates the state variables

$$P = \rho RT$$

- Where *R* is the "gas constant", which varies among the different gases
- The good news is that $R = R_d = 287$ J kg^{-1} K^{-1} for the dry air mixture

Partial Pressure, P

- The partial pressure P_x of a gas X in a mixture of gases of total pressure P is defined as the pressure that would be exerted by the molecules of X if all the other gases were removed from the mixture.

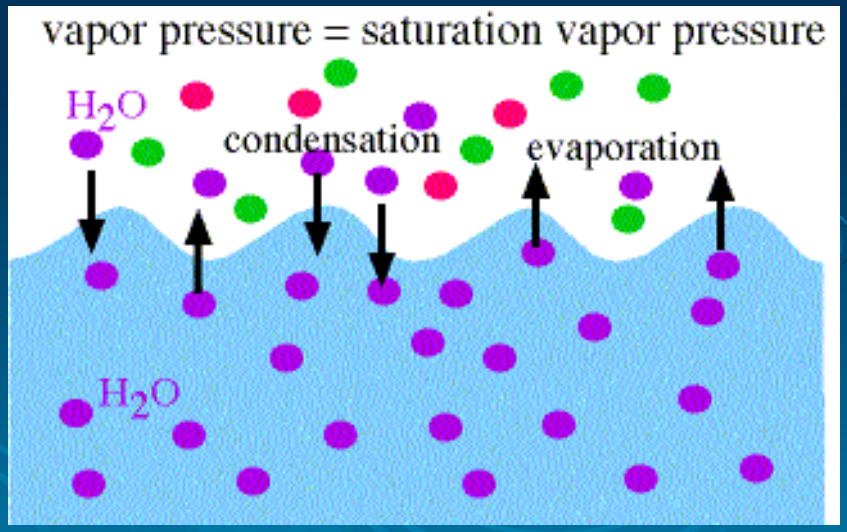


Vapor Pressure and Saturation

Another measure of the water vapor (moisture) content of the air can be obtained from the pressure exerted by the water vapor molecules themselves. All molecules in the air contribute to the total atmospheric pressure. That portion of the total pressure that is due only to that produced by the water vapor molecules is called the vapor pressure.

Evaporation of water molecules from an exposed body of liquid water will increase the number of water molecules in the air. The number of water molecules in the air will continue to increase until the rate at which evaporation is balanced by the rate at which water molecules in the air will return to the liquid water body (condensation)

When air is saturated, the pressure exerted by the water vapor, called the saturation vapor pressure, produces a balance between the number of water molecules leaving the surface of the water and the number returning.

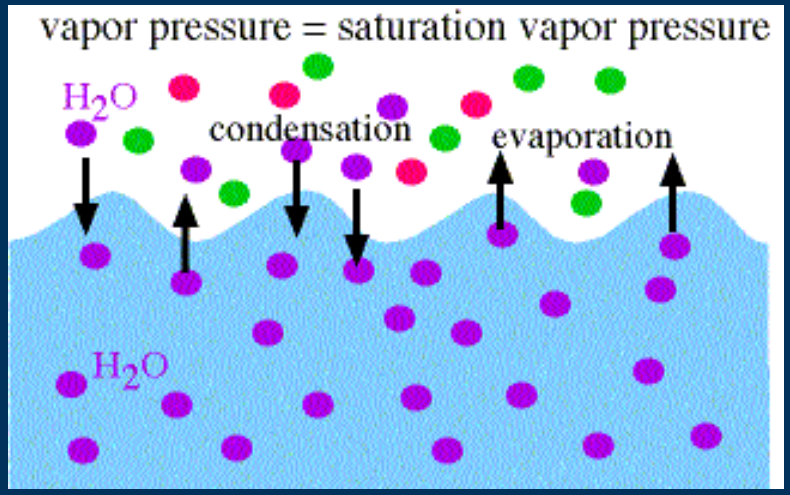


Saturation of Air

Air is **Saturated** if the abundance of water vapor (or any condensable) is at its maximum **Vapor Partial Pressure**.

In saturated air, ***evaporation is balanced by condensation***. If water vapor is added to saturated air, droplets begin to condense and fall out.

Under equilibrium conditions at a fixed temperature, the maximum vapor partial pressure of water is given by its **Saturated Vapor Pressure**.



http://apollo.lsc.vsc.edu/classes/met130/notes/chapter5/graphics/sat_vap_press.free.gif

Relative Humidity is the ratio of the measured partial pressure of vapor to that in saturated air, multiplied by 100.

The relative humidity in clouds is typically about 102-107%, in other words, the clouds are **Supersaturated**, by 2-7%.