

Lecture 4-5: The atmosphere.

Reading: Chapter 3 of Schlesinger

2nd HW set due Jan. 26, 2016

Ch. 3: The atmosphere.

1. The Earth's atmosphere is the least massive and most rapidly mixed global geochemical reservoir.
 - a. Mass $5.148 \pm .001 \times 10^{18}$ kg, variable due to water vapor
 - b. Mix time of lower atmosphere ~1 year (upper atmosphere slower)
 - i. – little geographic variation in composition (except H₂O)
 - c. Major constituents (ignoring H₂O vapor)
 - i. N₂ – 78%
 - ii. O₂ – 21%
 - iii. Ar – 0.9%
 - iv. CO₂ -- .039% (rising ~0.0002%/year)
 - v. H₂O – variable, typically ~1% at ground level
 - vi. Trace gasses – CH₄, H₂, N₂O, O₃, Ne, He, Kr, Xe, etc.

Average composition of dry atmosphere, by volume	
Gas	per NASA
Nitrogen , N ₂	78.084%
Oxygen , O ₂	20.946%
Argon , Ar	0.934%
Minor constituents (in ppm)	
Carbon Dioxide , CO ₂	383
Neon , Ne	18.18
Helium , He	5.24
Methane , CH ₄	1.7
Krypton , Kr	1.14
Hydrogen , H ₂	0.55
Water	
Water vapour	Highly variable; typically makes up about 1%

2. Basic chemistry of air – nearly ideal gas, $PV \approx nRT$
 - a. Expands on heating ($V \approx T$ at constant pressure)
 - b. Temp increases when air is compressed, drops when expanded
 $T_2/T_1 \approx (V_1/V_2)^{2/5}$ (dry, adiabatic – no heat added)
 - c. Capable of holding more H₂O at high T
 - i. Warming or descending air evaporates water
 - ii. Cooling or ascending air condenses water (clouds)

3. Structure of the atmosphere (Fig. 3.1)
 - a. Troposphere ~adiabatic (warm low, cold high)
 - i. Lowest ~10km of atm.
 - ii. 80% of atmospheric mass
 - b. Stratosphere – temperature inversion (warm high, cold low)
 - i. From 10km to ~50km
 - ii. Temperature inversion indicates poor mixing (no weather).
 1. ~75% replacement of air from troposphere per year
 - a. $MRT = \text{Mass}/\text{Flux}$
For stratosphere $MRT = 1/0.75 \approx 1.33$
 - iii. Chemistry a balance of input from below and reaction with sunlight & space energy (cosmic rays & etc.)
 1. Ozone (O₃) critical absorber of solar UV
 2. Ozone chemically unstable, susceptible to attack by active molecules & light.
 3. Ozone abundance balance between reactivity of O₂ and destruction to reform O₂
2. The troposphere
 - a. Vigorous convective circulation, three main bands per hemisphere.
 - b. Slower N/S equatorial exchange
 - c. MRT of constituents from abundance variability (fig 3.5)
 - d. MRT of water -- ~25mm average column density/2.7mm average daily precipitation ≈ 9.3 days
 - e. CFC's – long lived, able to make it to the stratosphere
 - i. Strategy for replacements?
 - f. Aerosols (soil, marine, volcanic, condensates – SO₂ → H₂SO₄)
3. Tropospheric chemistry
 - a. Chemical reactivity dominated by short-lived gasses
 - b. Ar inert, N₂ almost inert (lightning, N-fixers) O₂ generally needs activation
 - c. Trace biogenic gasses (CH₄, CO, hydrocarbons, nitrogen, sulfur)
 - i. Many reduced, but slow to react with hydrogen
 - d. Ozone in the troposphere
 - i. Pollution: produced by NO_x -- reactive N-bearing molecules (from fossil-fuel burning)
 1. $\text{NO}_2 + \text{UVsunlight} \rightarrow \text{NO} + \text{O}$
 2. $\text{O} + \text{O}_2 \rightarrow \text{O}_3$
 3. Reaction stoichiometry equivalent to $\text{NO}_2 + \text{O}_2 \leftrightarrow \text{NO} + \text{O}_3$, but kinetics (rate) not the same! Atomic O much faster to react than O₂!
 4. The net reaction does go backwards spontaneously, e.g.,
$$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$$
 5. Steady-state abundance of O₃ is controlled by a dynamic equilibrium : $\text{O}_3 = 0.021\text{ppm} \cdot [\text{NO}_2]/[\text{NO}]$

6. Ozone also reacts with sunlight back to $O_2 + O$, even without NO, but requires Ultraviolet light ($\lambda < 310\text{nm}$, $h\nu > 4\text{ eV}$)
 7. O released from ozone can be in an unstable electronic state (1D), reacts with H_2O to make $\bullet OH$
 - ii. $\bullet OH$ – atmospheric garbage incinerator.
 1. Attacks trace gasses like CO, CH_4 , NO_2 , SO_2 , oxidizes them to inert or water-soluble phases.
4. The atmospheric greenhouse.
- a. Given our distance from the sun and reflection of incident sunlight from clouds, etc., total average heating of the Earth from sunlight is about 69% of 340 W/m^2 , or 235 W/m^2 .
 - b. Without an atmospheric greenhouse, Earth would re-radiate this energy back to space, acting like a black-body, arriving at a steady-state balance of sunlight in vs. thermal blackbody out:
 - i. $j^* = \sigma T^4$, $j^* \approx 235\text{ W/m}^2$ (σ is the blackbody constant, $\approx 5.67 \times 10^{-8}\text{ W/m}^2\text{K}^4$)
 - ii. at steady state, $T \approx (j^*/\sigma)^{1/4} = 254\text{ K} !!$
 - iii. Also, peak wavelength of thermal radiation $\sim 2.9 \times 10^6/T$
 1. $2.9 \times 10^6/290 \approx 10,000\text{ nm}$, or $3 \times 10^{13}/\text{sec}$ -- Infrared
 - c. Absorption of thermal radiation by atmosphere prevents some blackbody energy from escaping.
 - i. Small molecules vibrate $\sim 10^{13}/\text{sec}$, perfect for absorbing/scattering thermal radiation.
 - ii. Any molecule in the atmosphere with more than 1 element or more than 2 atoms will contribute to the greenhouse.
 1. N_2 , O_2 , Ar?
 2. H_2O , CO_2 ?
 3. Ozone?

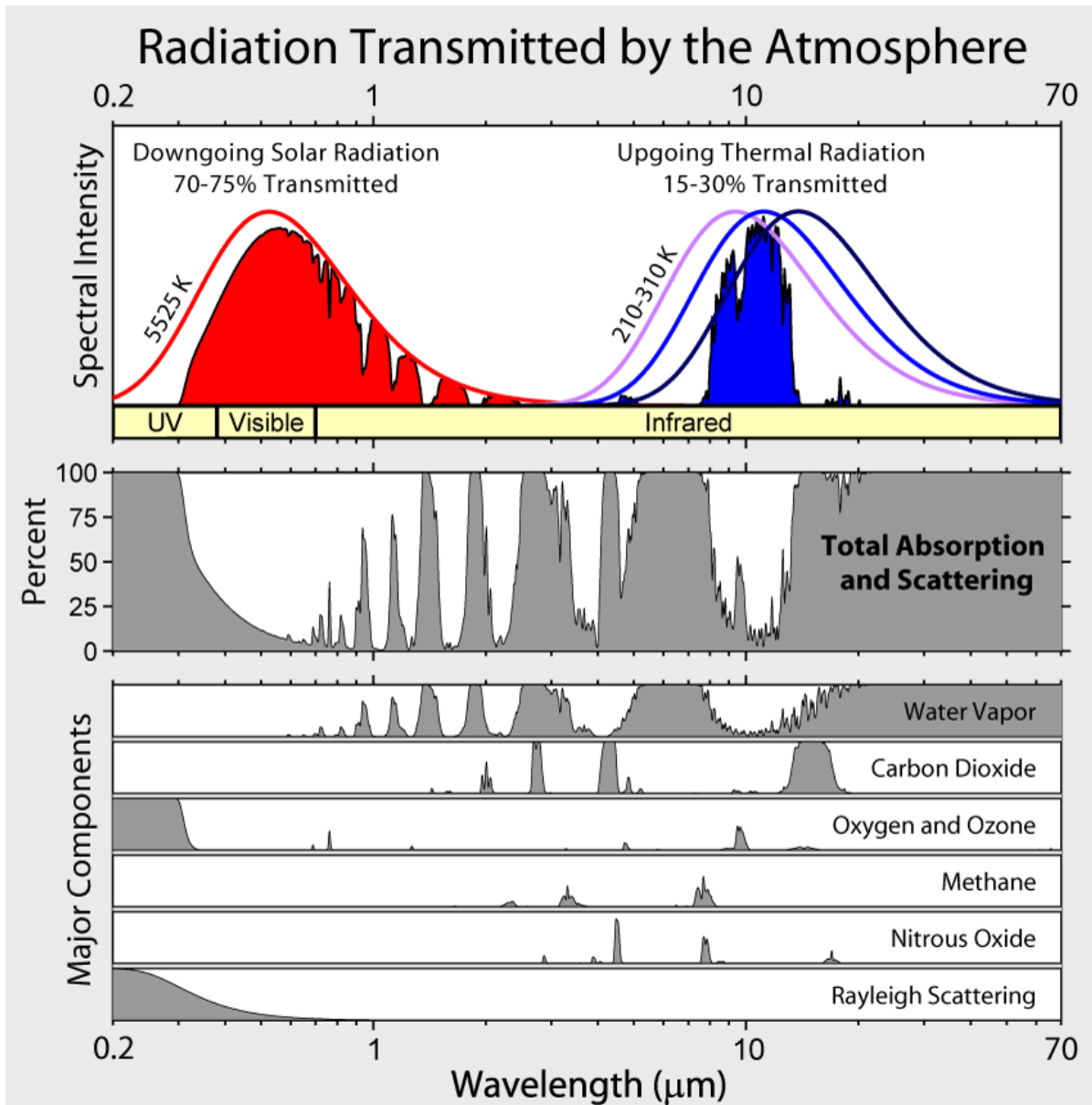


Figure by Robert A. Rohde, Global Warming Art Project, CC A Noncommercial S-A 2.5, http://commons.wikimedia.org/wiki/File:Atmospheric_Transmission.png

5. Atmospheric deposition

- a. Gases are lost not just to reaction, but also by transfer to condensed phases (precipitation, aerosols, direct dissolution/adsorption).
- b. Most pronounced for soluble gases (HNO_3 , H_2SO_4 , HCl , CO_2) and ions (Na^+ , Cl^- , Ca^{++})
- c. Lifetime of soluble gases tied to condensation of water – tend to be highly regional.