Atmospheric Chemistry and Physics

Nathan I. Hammer
Department of Chemistry & Biochemistry
University of Mississippi

- REFERENCES -

J. H. Seinfeld, and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley and Sons, 1998
R. P. Wayne, *Chemistry of Atmospheres*, Clarendon Press, 1985
D. J. Jacob, *Atmospheric Chemistry*, Princeton University Press, 1999

History

- 4.6 billion years ago – primordial solar nebula
- Atmosphere formed from release of trapped volatile compounds
    - CO_2
    - N_2
    - H_2O
    - H_2
- Early atmosphere similar to that emitted from today's volcanoes
- Water condensed to form oceans
- CO_2 dissolved in ocean to form sedimentary carbonate rocks
- N_2 stayed in the atmosphere since it didn't have anywhere to go
- Early atmosphere was reducing while present day is oxidizing

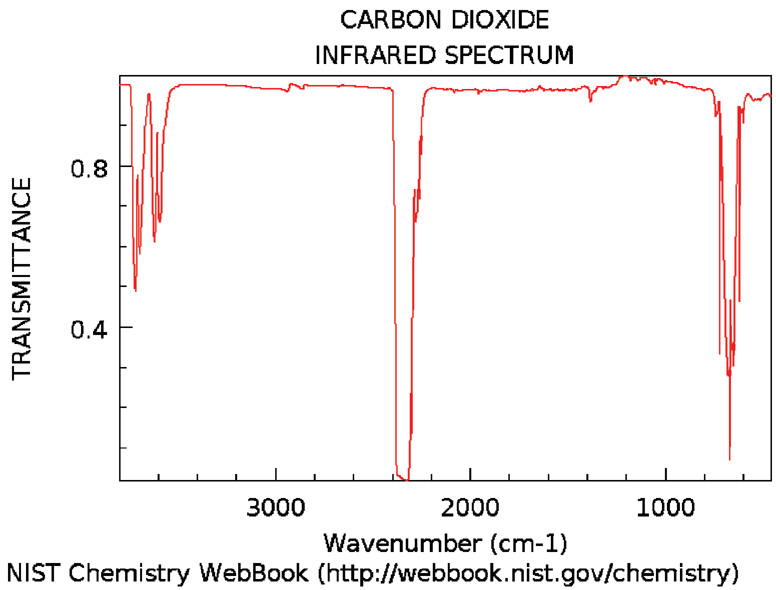
History, continued

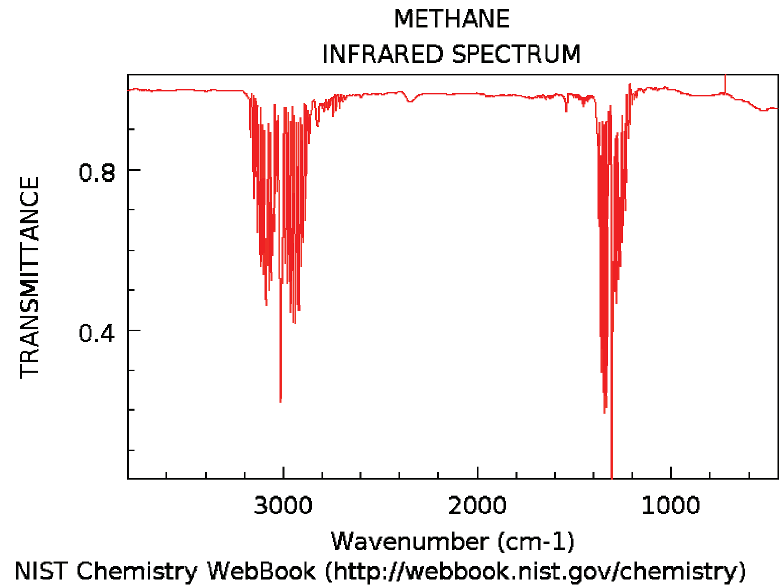
- O_2 came from photosynthesis
- Current level of O_2 was achieved 400 million years ago
- Current level of O_2 is maintained by balance of photosynthesis and respiration and decay of organic carbon
- If O_2 not replenished, surface organic carbon would be completely oxidized in 20 years – but still have 99+% of O_2 in the atmosphere

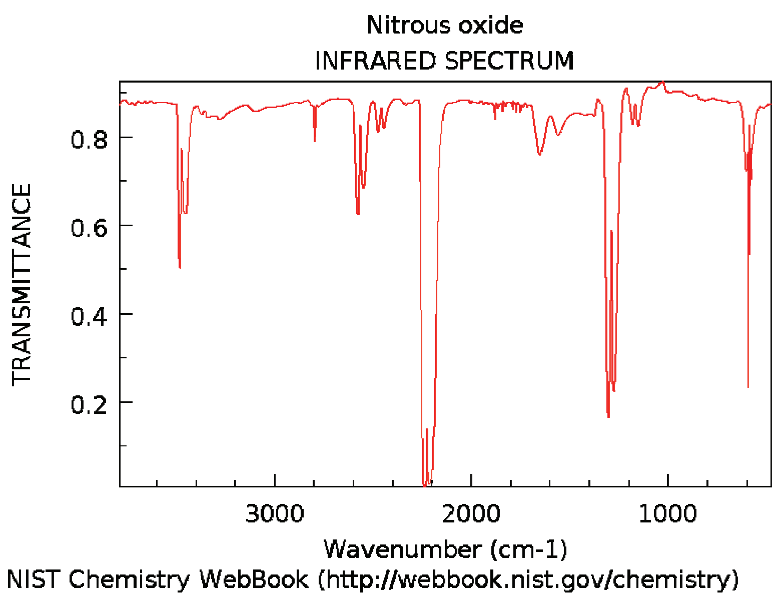
The Atmosphere Today

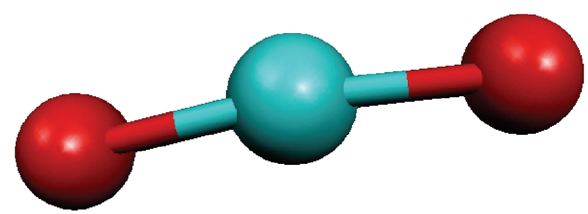
- N_2 (78%), O_2 (21%), Ar (1%)
- Abundances controlled by the biosphere, uptake and release from crustal material, and degassing of the interior
- Water vapor is next on the list and is found in the lower atmosphere where concentrations can reach 3% - Evaporation and Condensation
- All the rest of gases are trace gases
- Can detect trace gases down to at least 1 part per trillion (volume)
- Comparison with bubbles in ice cores reveal recent dramatic increases in the concentration of CH_4, CO_2, N_2O, and halogens
- These last species are green house gases

Infrared Absorption

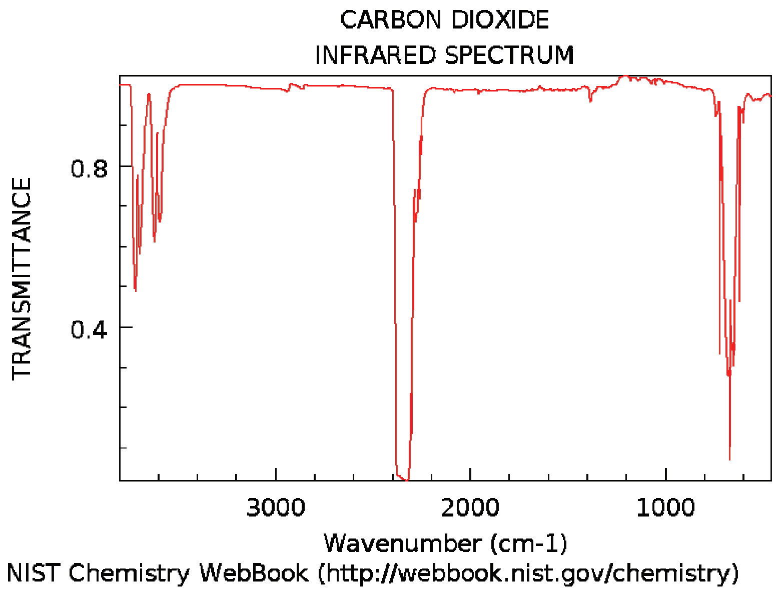


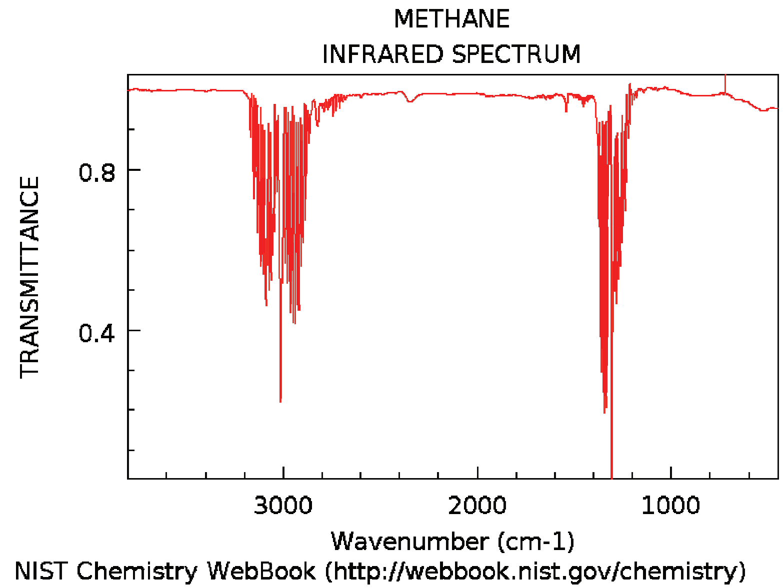


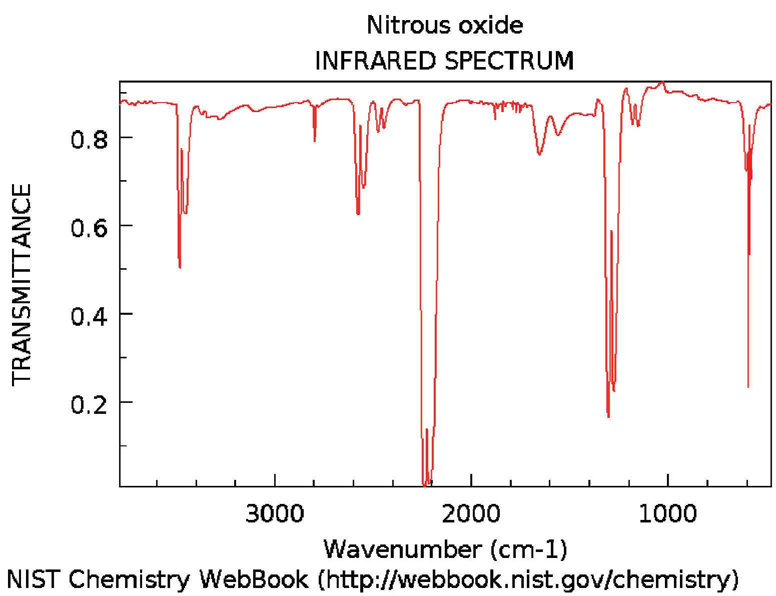


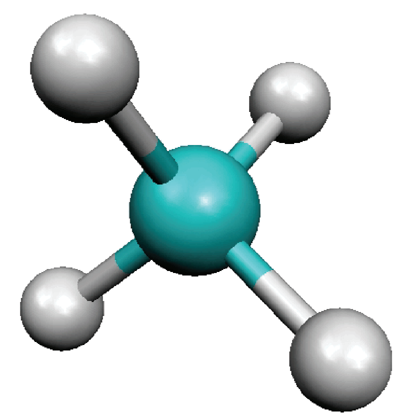


Infrared Absorption









The Atmosphere Today, continued

- Trace gases increase daily
- Products of fossil fuel combustion and by-products of chemical industry
- Introduction of new chemicals leads to problems – smog from automobile pollution (figured out in 1950s) and ozone depletion from chlorofluorocarbons (figured out in 1970s)
- The concentration of these chemicals is complicated
- Example: CH_4 is green house gas, removed by reaction with OH radical (rate depends on [OH]), [OH] depends on [CO], which is a product of CH_4 oxidation

Atmospheric Chemistry & Physics - Terms

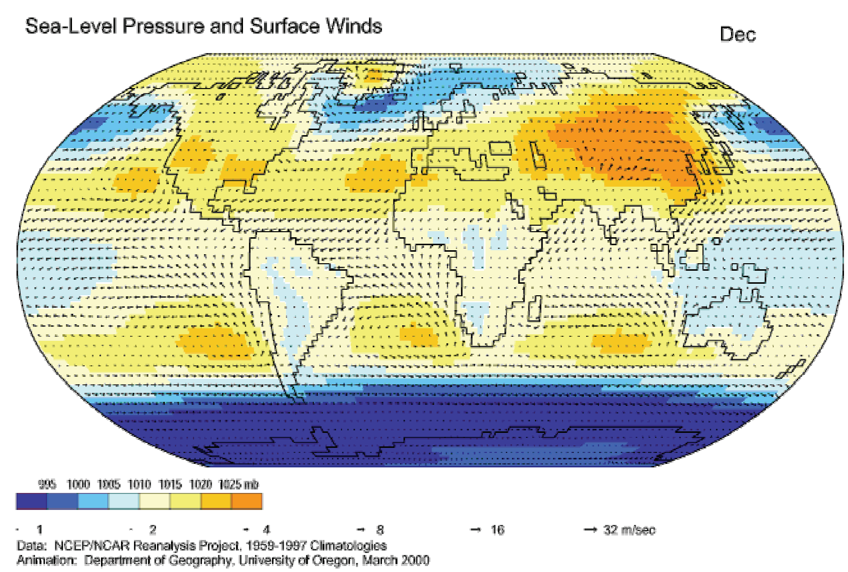
- **Steady State Concentrations**
- **Chemical Cycles**
- **Chemical Chains**
- **Transport**
- **Sink**
- **Dry deposition**
- **Wet deposition**
- **Annual Cycles**
- **Oxidation**
- **Models**

To calculate or measure an atmospheric property you must specify the temporal period and spatial extent of the measurement

Geostrophic Flow

- Air moves from high to low pressure
- Large scale movement of air driven by differential heating of Earth
- Coriolis Effect – Rotating Earth $F_c = 2\Omega V_h \sin\phi$
- Different pressures at different parts of the Earth's surface
- Atmospheric Circulation – transports energy polewards, thus reducing the resulting equator-to-pole temperature contrast. Hadley, Ferrel, Polar Cells.

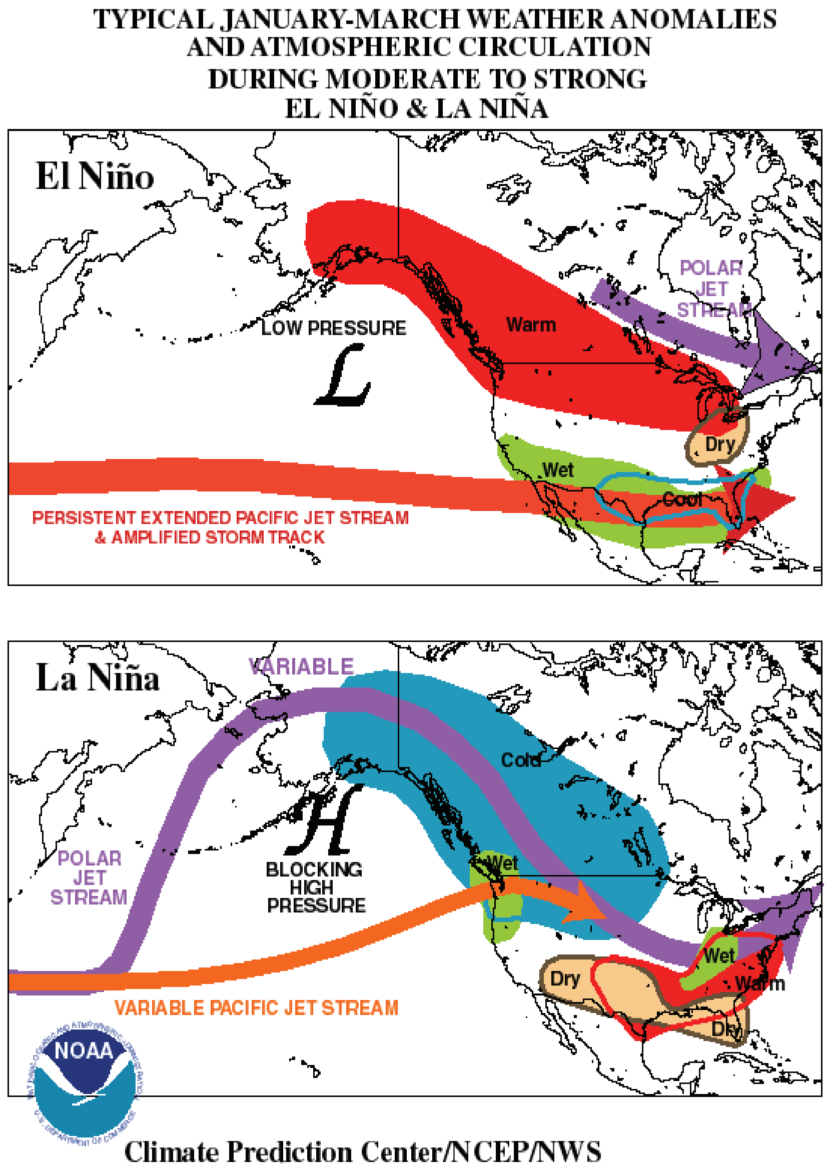
Source: http://en.wikipedia.org/wiki/Image:Coriolis_effect14.png



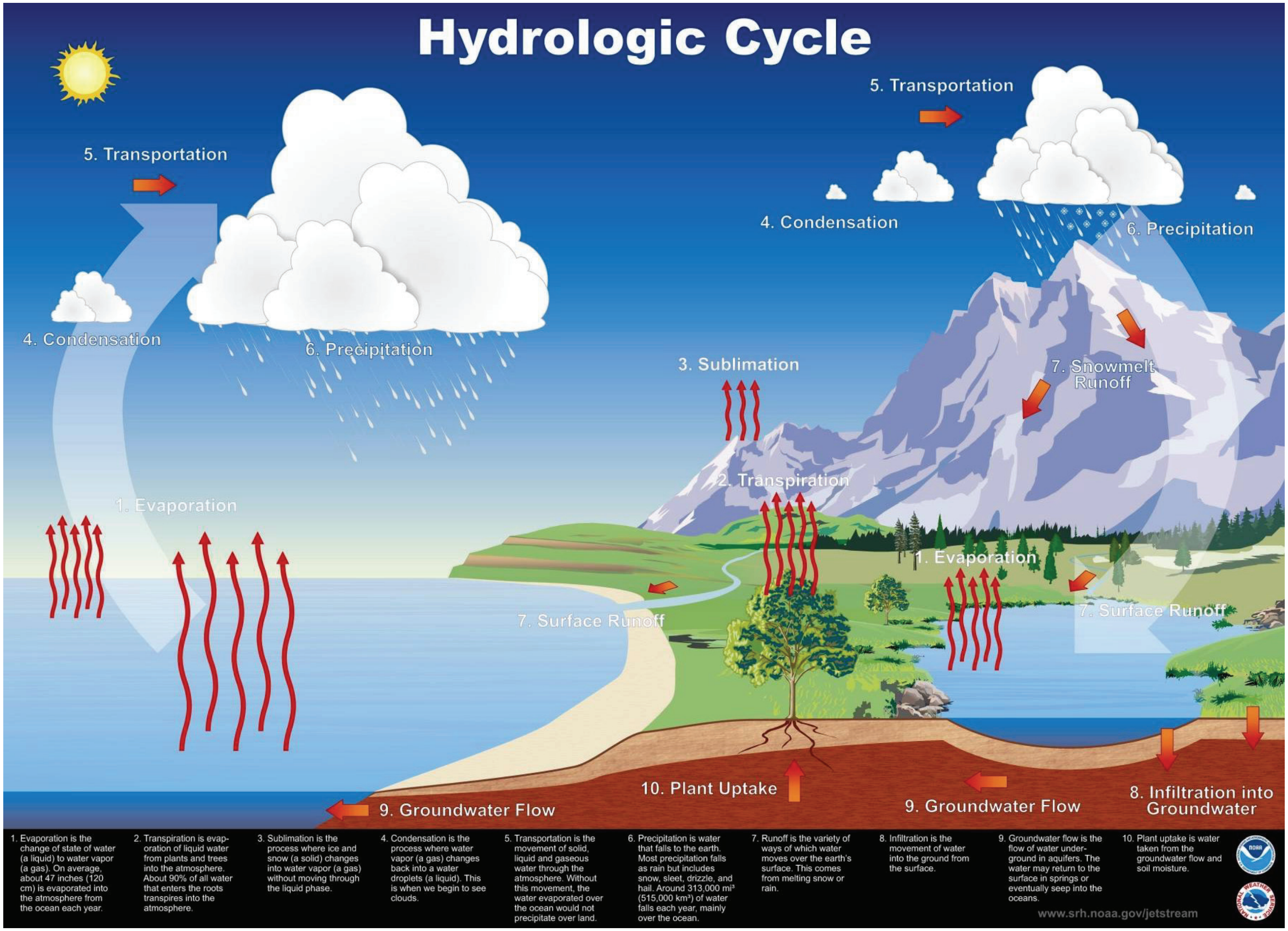
El Nino/Southern Oscillation and La Nina

- Fluctuation in atmospheric mass across Pacific
- El Nino – Warmer than normal air across the Pacific
- La Nina – Colder than normal air across the Pacific
- Last for 2 – 7 years
- Have global effects
- Affect jet stream across North America
- Thought to cause droughts, intense hurricane seasons, warmer and wetter winters
- Some believe that global warming will affect these cycles – people try to look for evidence

El Nino/Southern Oscillation and La Nina



Water Cycle



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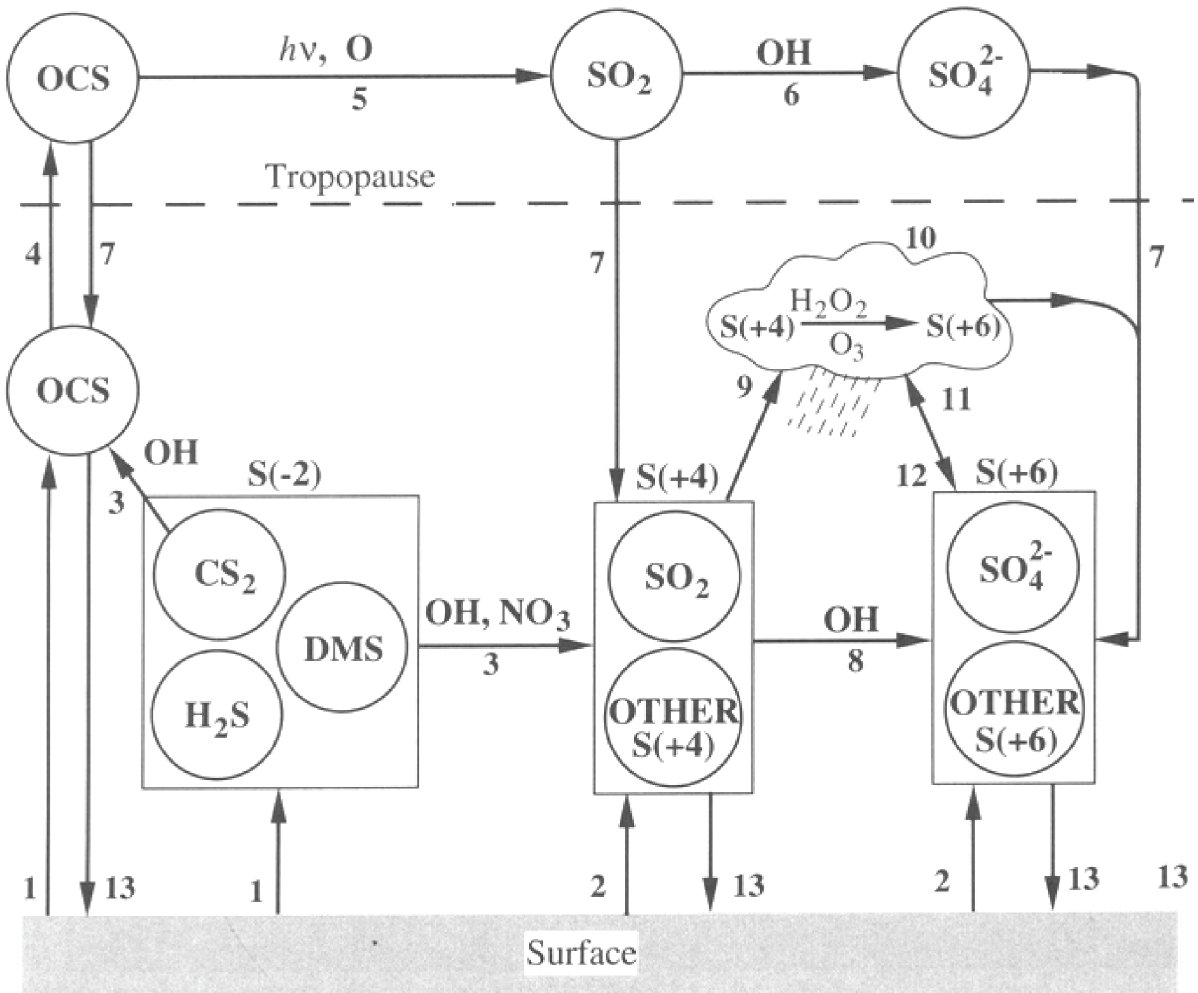
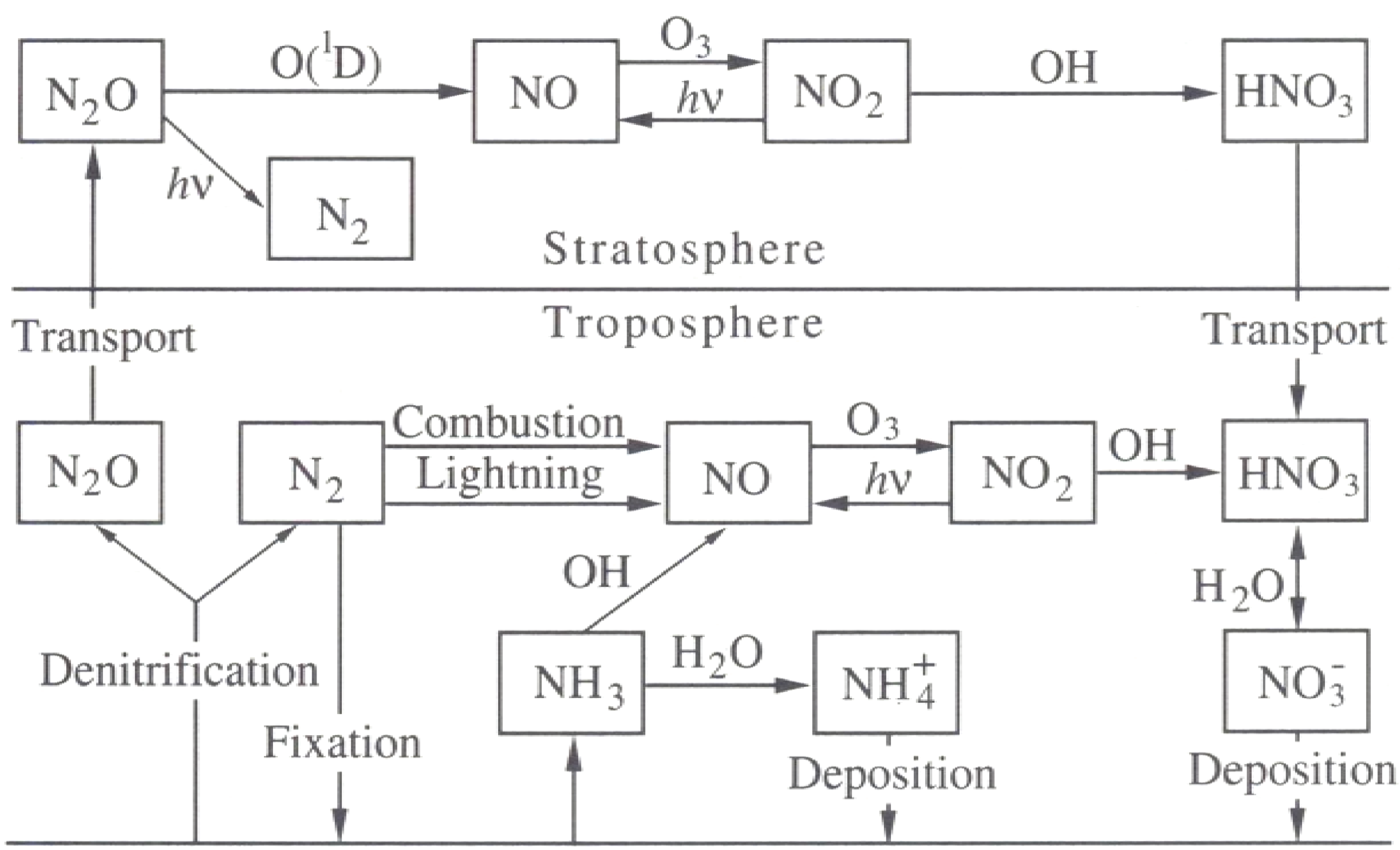
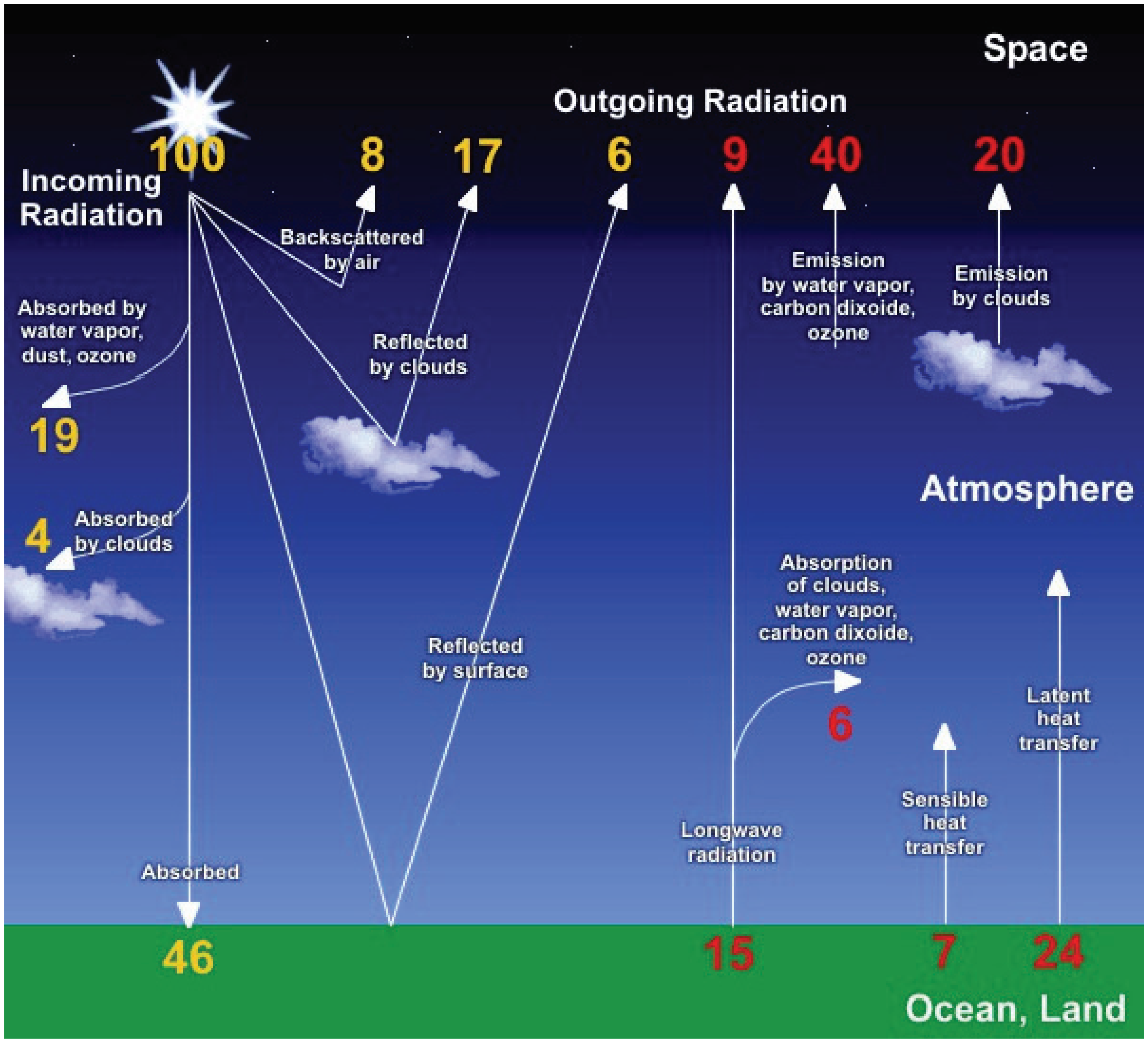
Major Pathways of Sulfur Compounds



Major Pathways of Nitrogen Compounds



Energy Cycle



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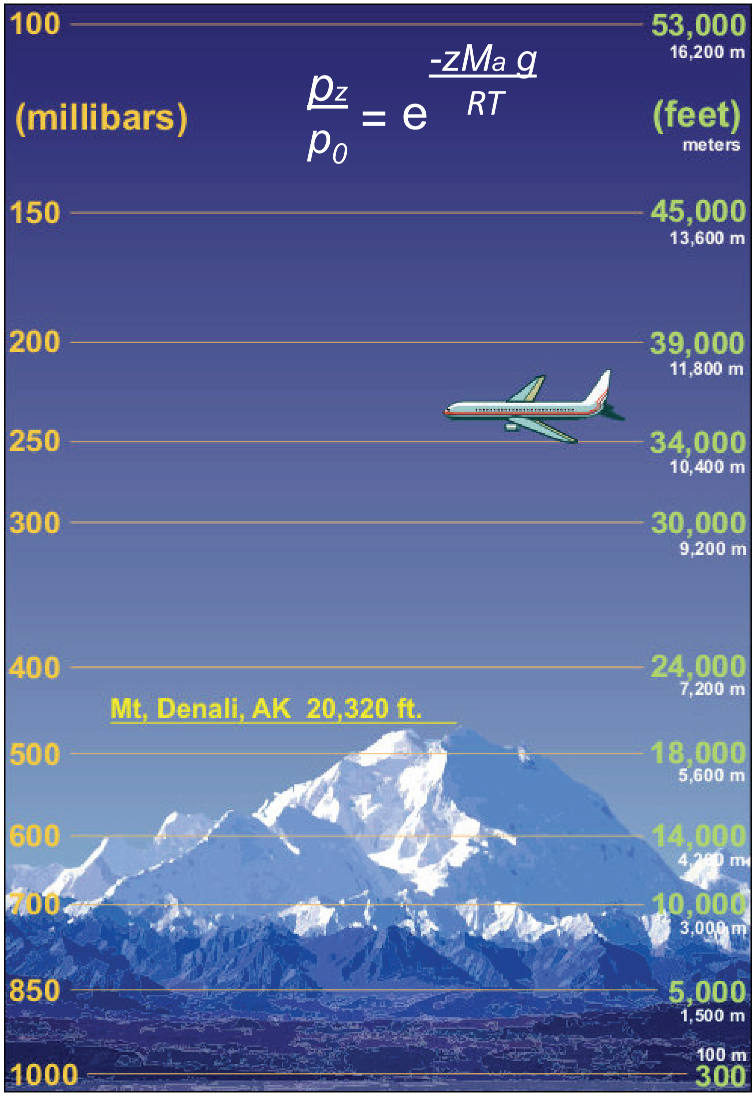
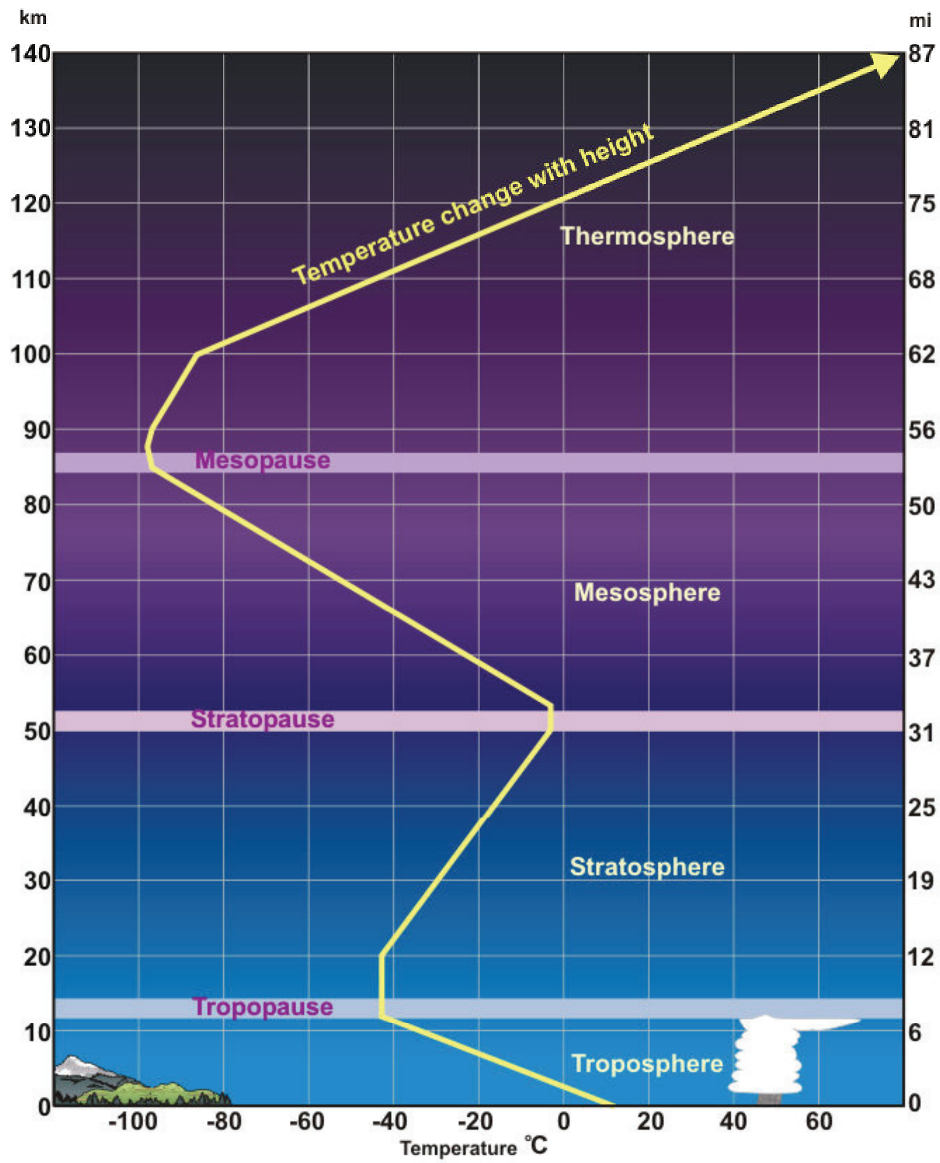
Layers of The Atmosphere





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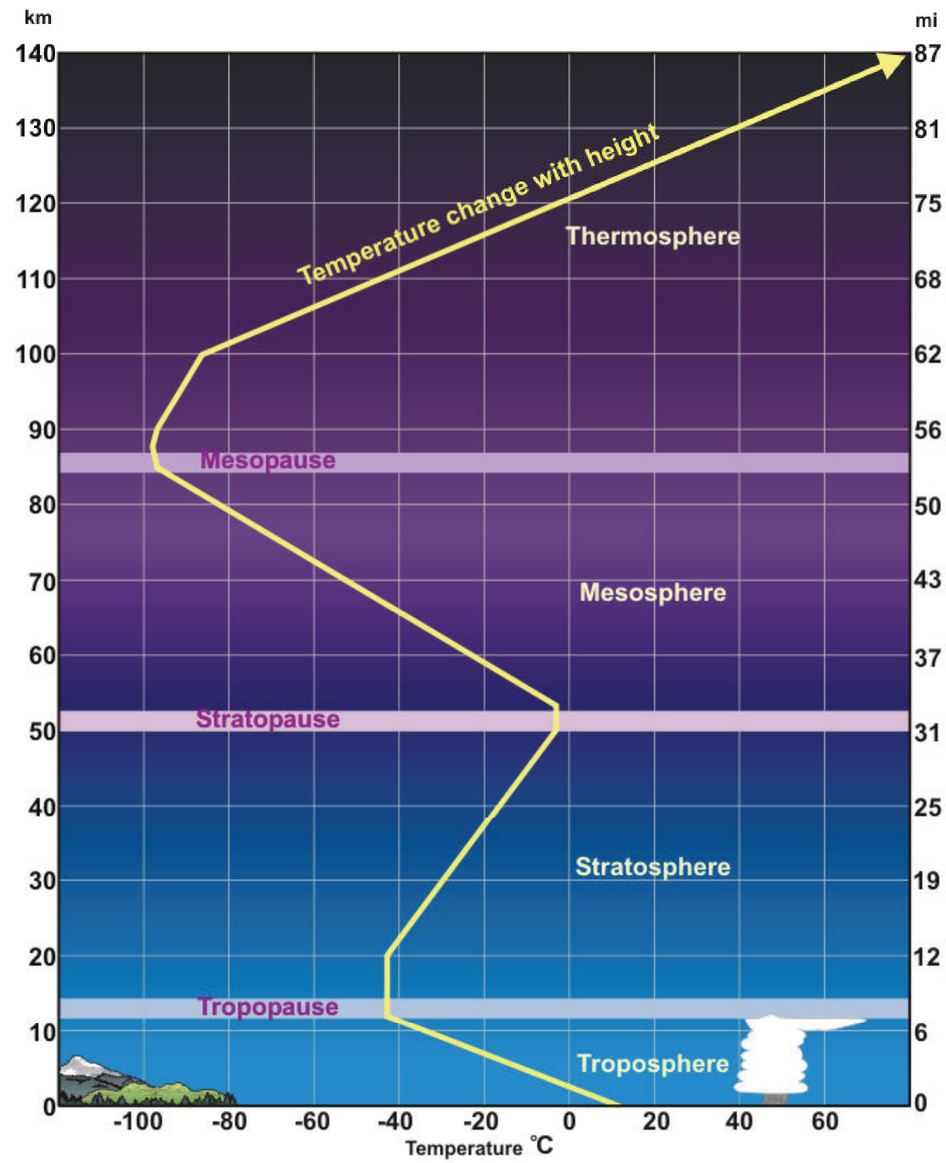
Layers of The Atmosphere

Ions…

Photochemistry of Small Diatomic Molecules, Reactions of atoms & ions

Ozone and Oxygen Dissociation, Nitric Oxide and CFC's, N_2 (79%), O_2 (21%), O_3 (1.3×10^{-5}), 200nm +

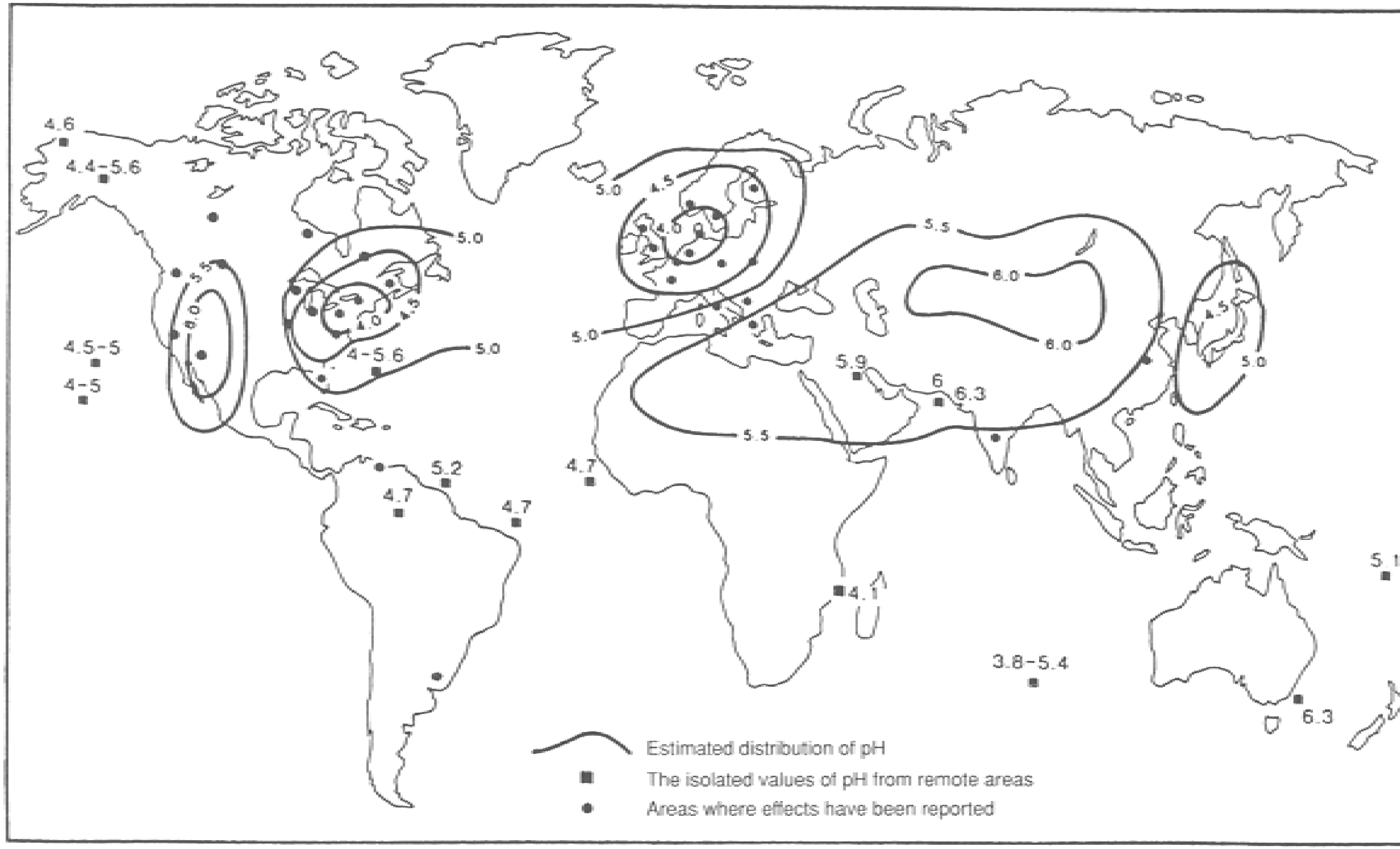
Acid Rain, photochemical smog… Visible and Infrared



Acid Rain

- SO_2 and NO_x get oxidized to sulfate and nitrate
- Organics get oxidizes to make organic acids
- Gas Phase: HNO_3, HCl, HCOOH, CH_3COOH, etc.
- Aerosol Phase: sulfate, nitrate, chloride, organic acids, etc.
- Acid deposition: wet and dry removal from atmosphere
- Acid rain is form of wet deposition
- Pollution free pH = 5.6 because of CO_2
- Lowered because of new species
- Acid rain began over 300 years ago in Europe – SO_2 from England traveled to France…
- High pH can occur due to alkaline dust deposits

Acid Rain


4.6
4.4–5.6
4.5–5
4–5
5.5
6.0
5.0
4.5
4.0
4–5.6
5.0
5.0
4.5
4.0
5.0
5.5
6.0
6.0
4.5
5.0
5.9
6
6.3
5.5
5.2
4.7
4.7
4.7
4.1
3.8–5.4
5.1
6.3
Estimated distribution of pH
The isolated values of pH from remote areas
Areas where effects have been reported

Smog

- Photochemical Smog
- London, Beijing, Mexico City, Tehran, Los Angeles, New York
- $NO_2 + h\nu \rightarrow NO + O$
- $O + O_2 + M \rightarrow O_3 + M$
- $NO + O_3 \rightarrow NO_2 + O_2$
- $RH + OH\cdot \rightarrow R\cdot + H_2O$
- $R\cdot + O_2 + M \rightarrow RO_2\cdot + M$
- $RCHO + OH\cdot \rightarrow RCO + H_2O$
- $RCO + O_2 + M \rightarrow RC(O)O_2 + M$
- etc.

Chemistry of Ozone

- Chapman Mechanism – 1930

  $O_2 + h\nu$ (< 200 nm) $\rightarrow 2O$

  $O_3 + h\nu$ (200 nm – 310 nm) $\rightarrow O_2 + O$

  $O + O_2 (+M) \rightarrow O_3 (+M)$

  $O + O_3 \rightarrow 2O_2$

- Chapman Mechanism predicts $[O_3]$ three times too big
- Other chemical mechanisms involving O_3 are present in the atmosphere

Chemistry of Ozone - Destruction

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

$O + O_3 \rightarrow 2O_2$

NO_x

$HO + O_3 \rightarrow HOO + O_2$

$HOO + O_3 \rightarrow HO + 2O_2$

$2O_3 \rightarrow 3O_2$

Hydroxyl Radical

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

$O_3 + O \rightarrow 2O_2$

CFC’s

Chemistry of Ozone - Creation

$$NO_2 + h\nu \rightarrow O + NO$$

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

$$OH + CO \rightarrow H + CO_2$$

$$H + O_2 + M \rightarrow HOO + M$$

$$HOO + NO \rightarrow OH + NO_2$$

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net: $CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$

Chemistry of Cl and O_3 – Ozone Hole

- **Polar vortex isolates the stratosphere over Antarctica**
- **During winter, ice and nitric acid trihydrate condense to form stratospheric clouds**
- **Crystals in clouds provide reactive surfaces that store $ClONO_2$**
- **When sun reappears in the spring the crystals melt and release Cl atoms (which destroy O_3) and ClO (see below)**

$$ClO + ClO \rightarrow Cl_2O_2$$

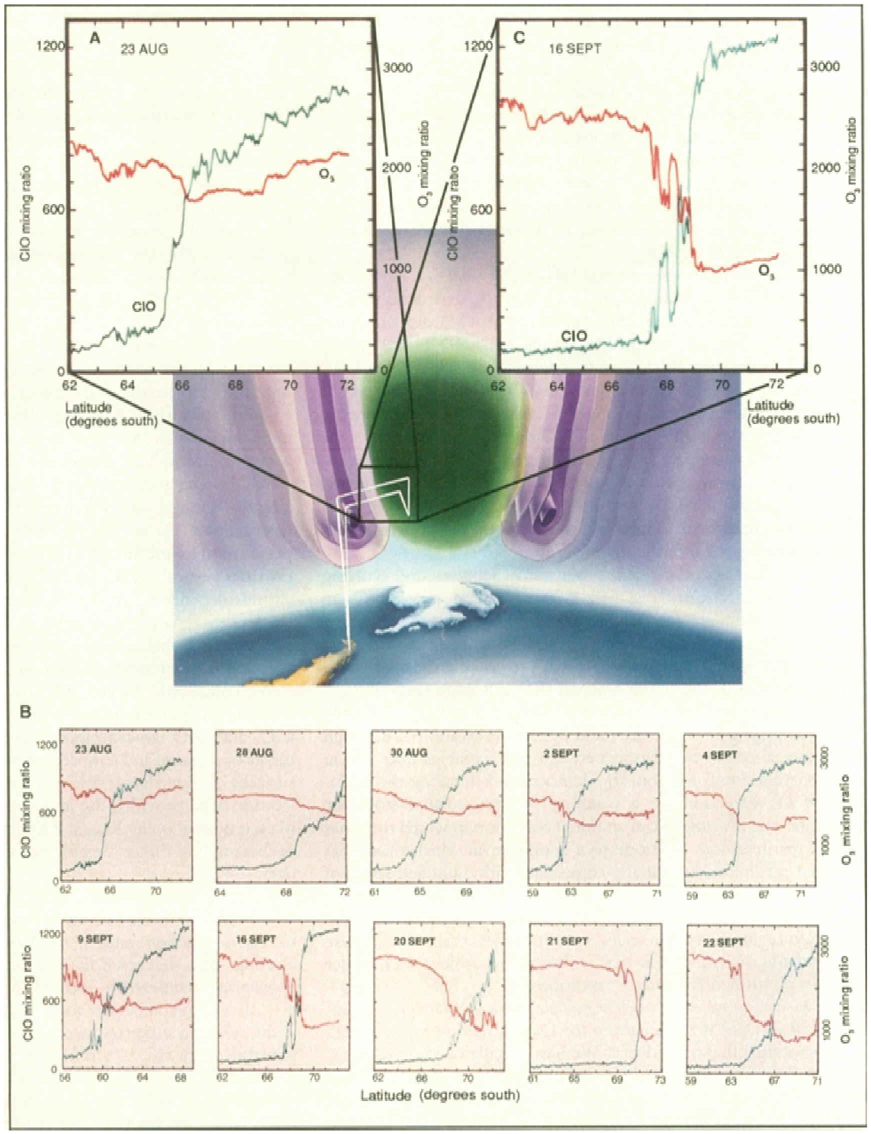
$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO$$

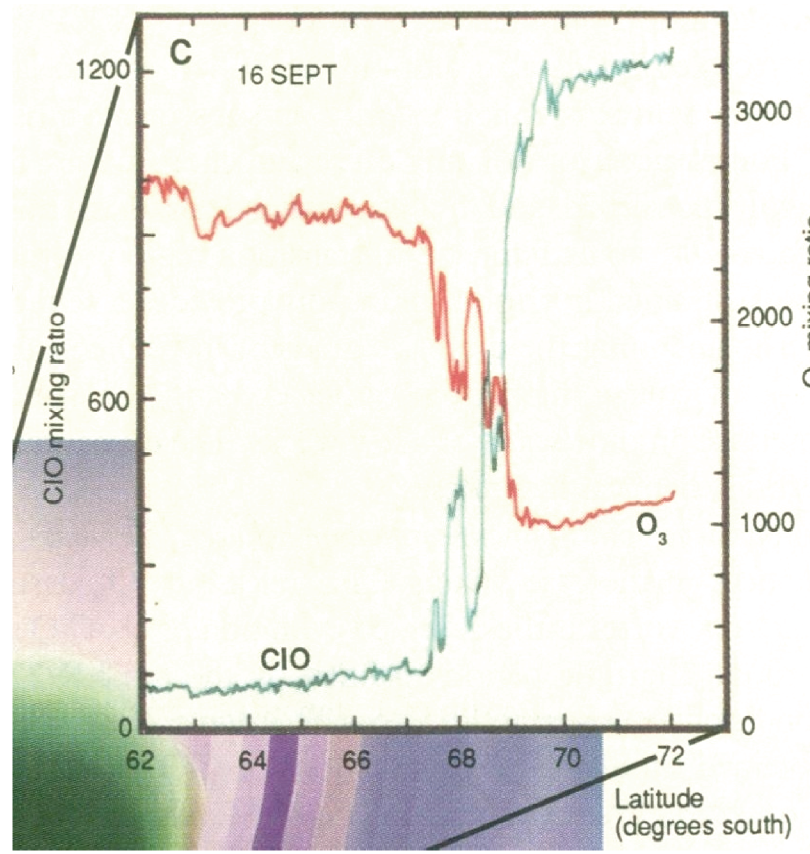
$$ClOO + M \rightarrow Cl + O_2 + M$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$2O_3 + h\nu \rightarrow 3O_2$$

Chemistry of Cl – Ozone Hole





J. G. Anderson, D. W. Toohey, and W. H. Brune, Science, **251**, 39 (1991)

Oxidation, Chains

$OH + CO \rightarrow H + CO_2$

$OH + CH_4 \rightarrow CH_3 + H_2O$

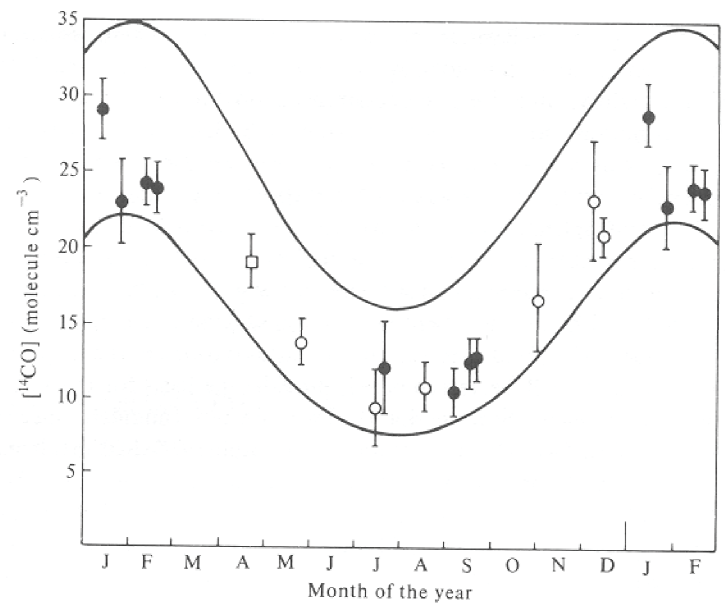
$H + O_2 + M \rightarrow HO_2 + M$

$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$CH_3O + O_2 \rightarrow HCHO + HO_2$

$HCHO + h\nu \rightarrow H + HCO$



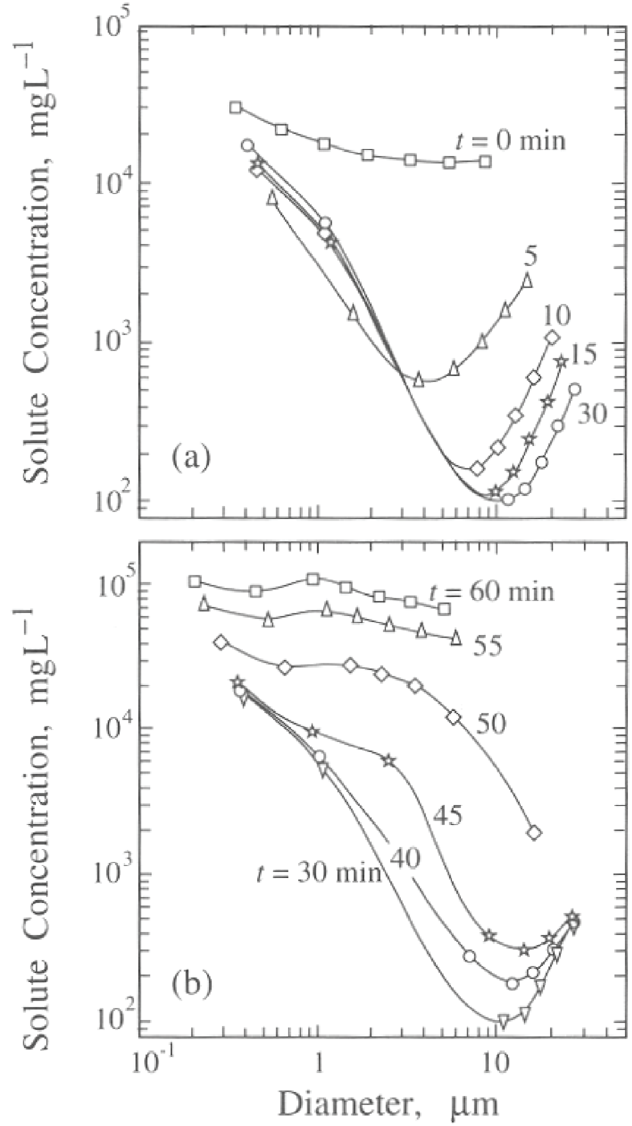
R. P. Wayne, *Chemistry of Atmospheres,* Clarendon Press, 1985.

formaldehyde

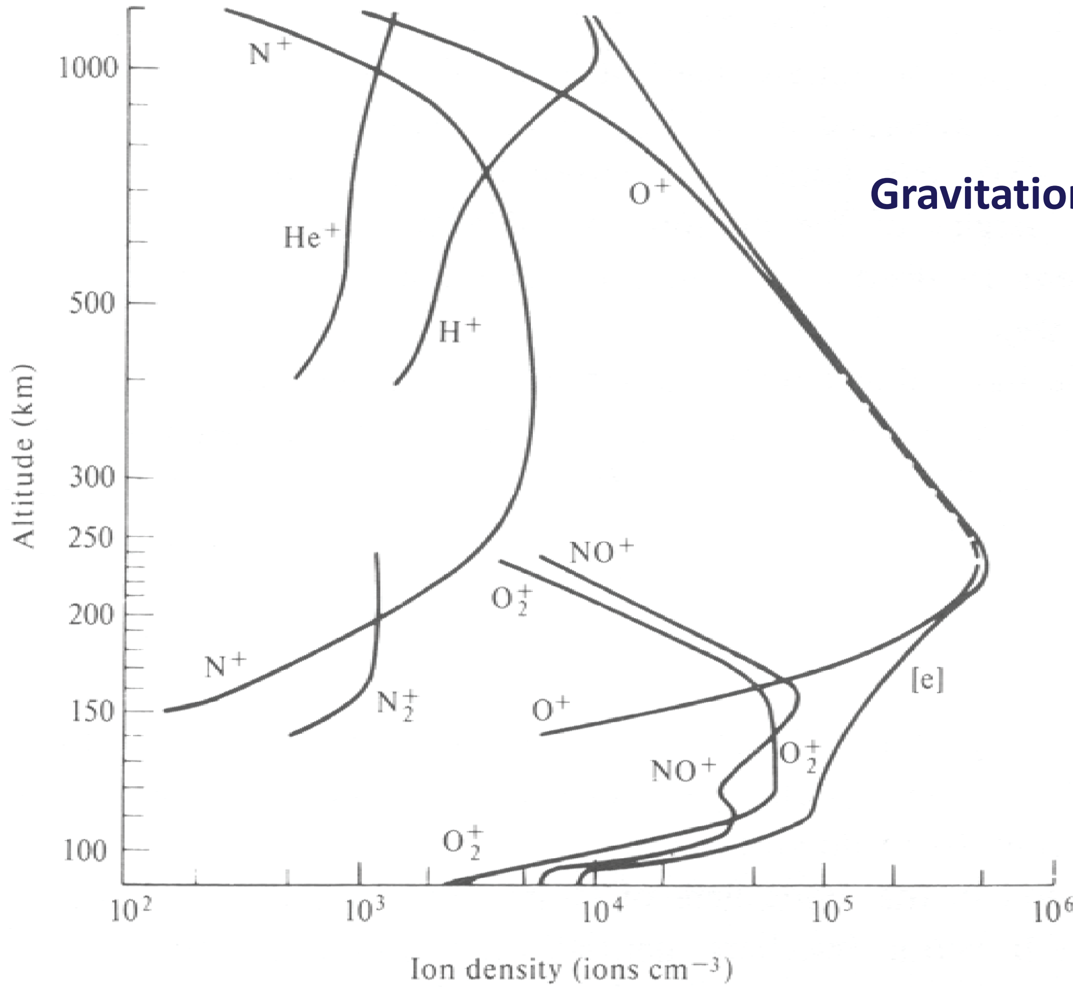
Works for higher hydrocarbons as well…

Aerosols

- Clouds form around particles in the atmosphere
- Different particles yield different droplet sizes
- Smaller droplets grow faster and dilute faster
- Aerosols span from a few nm to 100μ
- Aerosols come from combustion, dust, pollens, plant fragments, sea salts, etc.
- Size dictates chemical properties and lifetime in atmosphere



Ion Chemistry



Gravitational Separation

R. P. Wayne, *Chemistry of Atmospheres,* Clarendon Press, 1985.

Ion Chemistry

$O^+ + O_2 \rightarrow O + O_2^+$

$O_2^+ + e \rightarrow O^* + O$

$O^+ + N_2 \rightarrow N + NO^+$

$NO^+ + e \rightarrow N^* + O$

$N_2^+ + O \rightarrow N^* + NO^+$

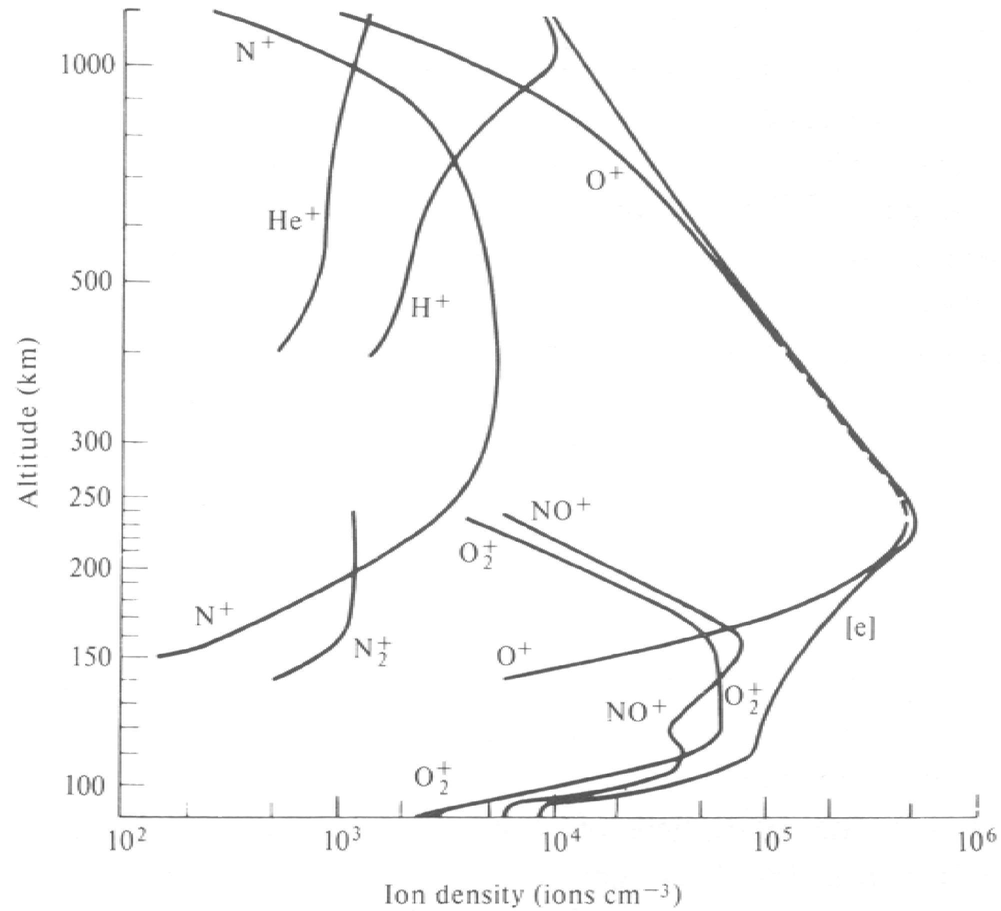
$N_2^+ + O_2 \rightarrow N_2 + O_2^+$

$O_2^+ + N_2 \rightarrow NO + NO^+$

$O_2^+ + NO \rightarrow O_2 + NO^+$

$H^+(H_2O)_n + e \rightarrow H + nH_2O$

$H^+(H_2O)_n + C \rightarrow H^+C(H_2O)_{n-1} + H_2O$



Atmospheric Models

- Transport Models
- Model Types – Mathematical or Physical
- Box Model
- Need to couple to ocean models and ice coverage models