Overview

Goal: Understand some of the basic principles of the chemistry of earth science and environment

- Knowledge necessary for solving current and emerging problems

Course of study:

1. What are chemical constituents of environment
2. How physical and chemical properties determine processes
   - Self-cleansing of troposphere
   - Smog
   - Acid rain
   - O_3 depletion
   - Global warming

Composition and Structure of Atmosphere

History: Paleoatmosphere (ancient atmosphere) very different from current atmosphere. Lets examine the evolution of atmosphere from a chemical perspective

1. Origin: Secondary origin-Gases trapped in interior of earth escape gradually to form atmosphere. Ex. CO_2 from carbonates in rocks
   - Primarily *not* due to gravitational collapse of elements in solar nebula
2. Cooling process $\longrightarrow$ water condensation to form oceans; critical for emergence of life
3. Atmosphere is mildly reducing (NH_3, CH_4 present)
4. Mostly N_2 with small amounts of H_2O and CO_2
5. Earth surface unshielded from UV rays $\longrightarrow$ only small molecules present
   - Key step: evolution of bacterial life from nucleic acids
   - Bacteria make O_2 which filters out UV rays $\longrightarrow$ evolution of complex organic molecules
   - Evolution of photosynthetic plants $\longrightarrow$ O_2 rich atmosphere
   - Evolution of Eucaryotic cells (have nucleus)
6. Atmosphere stabilizes and reaches an equilibrium until a particularly intrusive two-legged creature emerges

Constituents of Modern Atmosphere

- Dynamic system: coupled chemical processes $\longrightarrow$ rates of reactions of vital importance
  - Volatility-mobility of a gas increases as mass decreases
  - Residence time

$$\frac{\text{Amount of substance in atmosphere}}{\text{rate of outflow from atmosphere}}$$

  - Long residence time $\longrightarrow$ even distribution in system
- Useful picture: Sources and Sinks

Components

1. N_2: 78% by volume concentration
   - Residence time: 16,000,000 years
   - Sources:
     (a) Protein and nucleic acid breakdown
     (b) Fertilizer breakdown
   - Sinks:
     (a) Nitrogen fixation
     (b) Thunderstorms
     (c) Haber process: synthesis of fertilizers
2. O_2: 20.9% by volume
   - Sources:
     (a) Photosynthesis
     (b) Photolysis of ozone
   - Sinks:
     (a) Metabolism
     (b) Rusting and weathering
     (c) Burning: oxidation in atmosphere
3. Inert elements: Ar, Ne, He, Kr, Xe
   - Extremely unreactive-closed valence shells

- Exist as single atoms
- Created in early stages of universe via nuclear reactions

4. Water: roughly 0.0001 amount that is on land
   - Residence time: approximately 10 days $\longrightarrow$ unevenly distributed
   - Sources: many-some examples
     (a) Evaporation of lakes and rivers
     (b) Transpiration of trees and plants

5. Carbon monoxide CO: 0.1 ppm (part per million by volume)
   - Sources:
     (a) Decomposition of organic matter
     (b) Incomplete combustion
   - Sinks:
     (a) Micro-organisms
     (b) Hydroxy radical chemistry in troposphere

6. Carbon dioxide: CO_2 $318 - 350$ ppm
   - Sources:
     (a) Metabolism
     (b) Fossil fuels:coal combustion
   - Sinks:
     (a) Photosynthesis
     (b) Exchange with water bodies: CO_2 soluble in water

7. Methane: CH_4 1.7 ppm
   - Sources:
     (a) Anaerobic microbial decomposition
       - Ruminants are largest source!
       - Swamps and landfills
     (b) Natural gas pipelines
   - Sinks:
     (a) Burning: controlled and atmospheric

    (b) Hydroxy radical oxidation in troposphere
    (c) Bacterial consumption in soil
  - Rate of increase about 0.01 ppm/yr starting 150 years ago

8. Nitrogen compounds: NO_x, NH_3, N_2O
   - Natural sources:
     (a) Soils: bacterial decomposition
     (b) Lightning
     (c) Biological denitrification
   - Anthropogenic:
     (a) Transportation industry

Physical Structure of Atmosphere

- Physical characteristics of atmospheric regions *very* important in determining chemistry
- Examine chemistry occuring in physical regions of atmosphere

Division of Atmosphere:

1. Troposphere: (0-12 km)
   - 80% of mass of atmosphere
   - Turbulent due to heat of earth's surface: lots of mixing $\longrightarrow$ giant chemical reactor
   - Clouds and rain important in cleansing of atmosphere
   - Jet stream in upper troposphere important in chemical transport
   - Chemistry particularly relevant for:
     (a) Greenhouse effect
     (b) Smog
     (c) Acid rain
2. Tropopause: 16-18 km near equator to 8-12 km near poles
   - Little vertical mixing of air $\longrightarrow$ buffer to upper atmosphere
3. Stratosphere: 30-50 km

- Chemical compounds tend to stay
- Low density, small molecules
- UV absorption and ozone layer
- Relevant chemistry: ozone chemistry and depletion of ozone layer

4. Thermosphere: 50 km+
   - Mainly atomic elements in energetic states
   - Very low density
   - Non-equilibrated system

Temperature Profile:

1. Peak near stratosphere due to increased absorption of UV rays
   - Photochemistry $\longrightarrow$ heat
2. Temperature drops due to few UV rays, reduced photochemical activity
3. Greenhouse gases absorb and re-emit IR radiation from earth