

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 \rightarrow 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 \rightarrow only small molecules present
 - Key step: evolution of bacterial life from nucleic acids
 - Bacteria make O_2 which filters out UV rays \rightarrow evolution of complex organic molecules
 - Evolution of photosynthetic plants \rightarrow 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 → 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 → 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 → 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 occurring 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 → 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 → 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 \rightarrow heat
2. Temperature drops due to few UV rays, reduced photochemical activity
3. Greenhouse gases absorb and re-emit IR radiation from earth