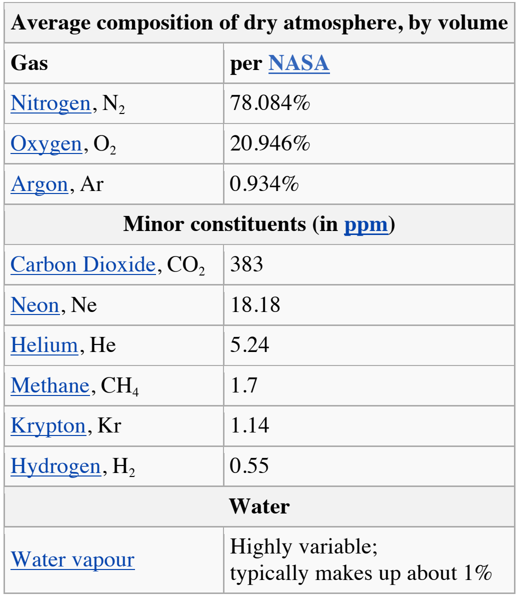
EPSS C113/213 Biological and Environmental Chemistry
Jan 19, 2018

Lectures 3: Evolution of metabolism, the atmosphere.
Reading: Chapter 2 and 3 of Schlesinger

1. Origin of organic molecules
    a. Exploitation of surface element reservoirs (general focus on most abundant elements).
    b. Special "polymer" chemistry of carbon, information, functionality optimization of complex C-C chains and rings.
    c. Carbon chemistry supplemented by elements with similar & higher electronegativity (N, H, O) – chain-compatible elements
2. Origin of metabolism
    a. All metabolic activity requires input of energy
        i. Photosynthesis – E from light
        ii. Chemosynthesis – E from chemical disequilibrium in environment
        iii. Heterotrophy – E from other organisms
    b. Early Earth probably had small reservoirs of free organic molecules (e.g., CH_3COOH, amino acids), from either extraterrestrial sources (meteorites, comets) or terrestrial sources (lightning, hydrothermal reactions, etc.)
    c. Atmosphere & oceans lacked free O_2, increasing lifetimes of organic molecules.
        i. Spontaneous exploitable disequilibria
            1. $CH_3COOH \rightarrow CO_2 + CH_4$ (Methanogenesis 1)
    d. Initial chemosynthesis also possibly based on spontaneous disequilibria
            1. $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (Methanogenesis 2)
        ii. Modern habitats?
    e. Photosynthesis – harvesting energy from sunlight, and storing it by *molecular separation* of oxidants and reducers.
        i. Oxidant: substance that tends to react by taking electrons.
           $O^0_2 + 4e^- \rightarrow 2O^{2-}$
        ii. Reducers: substance that tends to react by giving up electrons.
           $H^0_2 \rightarrow 2H^+ + 2e^-$
        iii. Combining an oxidant with a reducer liberates energy. Conversely, energy is required to separate them.
           $2H_2 + O_2 \rightarrow H^{(+)}_2O^{(2-)}$

Quantifying energy (thermodynamics) Reactions "go" spontaneously if their free energy is negative. I.e., the total free energy of the products (right side) must be lower than the total free energy of the reactants (left side) (See HW).
Ch. 3: The atmosphere.

1. The Earth's atmosphere is the least massive and most rapidly mixed global geochemical reservoir.
    a. Mass 5.148±.001 x 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 H_2O)
    c. Major constituents (ignoring H_2O vapor)
        i. N_2 – 78%
        ii. O_2 – 21%
        iii. Ar – 0.9%
        iv. CO_2 -- .039% (rising ~0.0002%/year)
        v. H_2O – variable, typically ~1% at ground level
        vi. Trace gasses – CH_4, H_2, N_2O, O_3, 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 H_2O 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