Atmospheric Chemistry

Spring 2014

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Atmospheric Pressure Units

- Force = mass x acceleration (g cm sec^{-2})
- Pressure = Force per unit area (g cm sec^{-2} cm^{-2}= g $cm^{-1}sec^{-2}$)
- Basic unit (SI): 1 Pascal = 1 kg $m^{-1}sec^{-2}$ = 10 g $cm^{-1}sec^{-2}$
- Earth's atmospheric pressure ~$1.013x10^{5}$ Pascals
  - = 1013 hectoPascals (hPa)
  - = 1013 millibars (mbar)
  - = 1 atmosphere

Pressure Distribution with Altitude

- Consider a slab of atmosphere of area, A, and thickness dz
- Upward force at top to hold up rest of atmosphere = $P(z+dz)*A$
- Downward force at bottom = $P(z)*A$
- Difference has to be weight of slab of thickness dz = $m*n*g*A*dz$
  - m is weight of molecule
  - n is density of molecules per cm^3
  - g is acceleration of gravity
- Thus $(P(z+dz)-P(z))/dz = dP/dz = -mng$
- Ideal gas law for unit volume; $P = nkT$
  - k is Boltzmann's constant $1.38\mathrm{x}10^{-16}$ cm^2 g sec^{-2} K^{-1}
  - T is temperature in Kelvin, K
- Solve for $n = P/kT$ and substitute
- $dP/P = -\ mg/kT*dz = -dz/H$ where H is called scale height
- Thus $P=P_0\exp(-z/H)$; pressure falls off with scale height H

Examples of Scale Height

- Surface T=288K, m=28.9x1.67e-24, g=980

  kT/mg =1.38e^{-16}*288/28.9/1.67e-24/980.= 8.4x10^{5} cm = 8.4 km

- Lower stratosphere T=220K

  kT/mg = 6.4 km

- Thermosphere at 200 km

  kT/mg = 30-100 km (solar min to solar max; or even day to night)

Some simple facts from kinetic theory of gases: Mean molecular velocity

Kinetic energy of molecules and temperature

$$\frac{m\overline{v^2}}{2} = \frac{3kT}{2}$$

Solve for mean speed

$$(\overline{v^2})^{\frac{1}{2}} = \left(\frac{3kT}{m}\right)$$

Substitute numbers for N_2 *at 230K*

$$(\overline{v^2})^{\frac{1}{2}} = \left(\frac{3 \cdot 1.38 \times 10^{-16} \cdot 230}{28 \cdot 1.67 \times 10^{-24}}\right)^{\frac{1}{2}} = 4.5 \times 10^4 \quad cm \cdot sec^{-1}$$

Some simple facts from kinetic theory of gases: Collision Frequency

Consider molecule with radius r and speed v. It will sweep out a cylinder of area $2\pi r^2$ *and length v in a unit of time. Thus the collision frequency will be the volume of this cylinder times the density of collision partners within the cylinder.*

$$\nu = \pi r^2 v n \quad sec^{-1}$$

With corrections for moving, finite-area partners

$$\nu = 2\sqrt{2}\,\pi r^2 v n \quad sec^{-1}$$

$$\nu = 2 \cdot \sqrt{2} \cdot 3.14 \cdot 3 \times 10^{-8} \cdot 3 \times 10^{-8} \cdot 4.5 \times 10^4 \cdot 10^{18} = 3.5 \times 10^8\, sec^{-1}$$

About 350 million collisions per second !

Some simple facts from kinetic theory of gases: Mean Free Path

Average distance between collisions

$$MFP = \frac{v}{\nu}$$

Example; N_2 at 230K and 10^{18} molecules cm^{-3}

$$MFP = \frac{4.5 \cdot 10^4}{3.5 \cdot 10^8} = 1.3 \cdot 10^{-4} cm = 1.3 \cdot 10^4 \mathring{A}$$

Bimolecular Reactions: Reaction Rate Coefficient

$$A + B \rightarrow AB \rightarrow C + D$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$\frac{dn(A)}{dt} = -kn(A) \cdot n(B)$$

Units of k are $cm^3sec^{-1}molecule^{-1}$

If every collision led to reaction go back to collision frequency and divide out the n → $\sim 3.5 \times 10^{-10}$ *for k*

Bimolecular Reactions: Reaction Rate Coefficient

- Most reactions do not occur on every collision
- Steric factors: reaction may depend on which direction A collides with B
- Activation energy: many reactions require energy to overcome repulsive barrier between molecules: leads to temperature-dependent reaction rate of form $\exp(-\Delta E/T)$