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 cm³
  - g is acceleration of gravity
- Thus (P(z+dz)-P(z))/dz = dP/dz = -mng
- Ideal gas law for unit volume; P = nkB
  - k is Boltzmann’s constant 1.38x10⁻¹⁶ cm² 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=P₀exp(-z/H); pressure falls off with scale height H
Examples of Scale Height

- Surface $T=288\,K$, $m=28.9 \times 1.67 \times 10^{-24}$, $g=980$
  \[ kT/mg = 1.38 \times 10^{-16} \times 288 / 28.9 / 1.67 \times 10^{-24} / 980. = 8.4 \times 10^5 \]
  \[ \text{cm} = 8.4 \text{ km} \]

- Lower stratosphere $T=220\,K$
  \[ kT/mg = 6.4 \text{ km} \]

- Thermosphere at 200 km
  \[ kT/mg = 30-100 \text{ km} \ (\text{solar min to solar max; or even day to night}) \]
Some simple facts from kinetic theory of gases: Mean molecular velocity

Kinetic energy of molecules and temperature

\[ \frac{mv^2}{2} = \frac{3kT}{2} \]

Solve for mean speed

\[ (\bar{v}^2)^{\frac{1}{2}} = \left( \frac{3kT}{m} \right) \]

Substitute numbers for \( N_2 \) at 230K

\[ (\bar{v}^2)^{\frac{1}{2}} = \left( \frac{3 \cdot 1.38 \times 10^{-16} \cdot 230}{28 \cdot 1.67 \times 10^{-24}} \right)^{\frac{1}{2}} = 4.5 \times 10^4 \text{ cm \cdot sec}^{-1} \]
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.

$$\nu = \pi r^2 vn \ sec^{-1}$$

With corrections for moving, finite-area partners

$$\nu = 2\sqrt{2} \pi r^2 vn \ sec^{-1}$$

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

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\(^{-3} \)

\[ MFP = \frac{4.5 \cdot 10^4}{3.5 \cdot 10^8} = 1.3 \cdot 10^{-4} \text{ cm} = 1.3 \cdot 10^4 \text{ Å} \]
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 \( cm^3\text{sec}^{-1}\text{molecule}^{-1} \)*

*If every collision led to reaction go back to collision frequency and divide out the \( n \) \( \rightarrow \sim 3.5 \times 10^{-10} \) 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 $\exp(-\Delta E/T)$