

# **Atmospheric Chemistry**

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# Atmospheric Pressure Units

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

# Pressure Distribution with Altitude

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- 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  $\text{cm}^3$
  - $g$  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  $1.38 \times 10^{-16} \text{ cm}^2 \text{ g sec}^{-2} \text{ K}^{-1}$
  - $T$  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

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- Surface  $T=288\text{K}$ ,  $m=28.9 \times 1.67 \times 10^{-24}$ ,  $g=980$   
 $kT/mg = 1.38 \times 10^{-16} \times 288 / (28.9 \times 1.67 \times 10^{-24} / 980) = 8.4 \times 10^5$   
cm = 8.4 km
- Lower stratosphere  $T=220\text{K}$   
 $kT/mg = 6.4$  km
- Thermosphere at 200 km  
 $kT/mg = 30\text{-}100$  km (solar min to solar max; or even day to night)

# Some simple facts from kinetic theory of gases:

## Mean molecular velocity

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*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<sub>2</sub> at 230K*

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

# Some simple facts from kinetic theory of gases: Collision Frequency

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*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.*

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

*With corrections for moving, finite-area partners*

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

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

*About 350 million collisions per second !*

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

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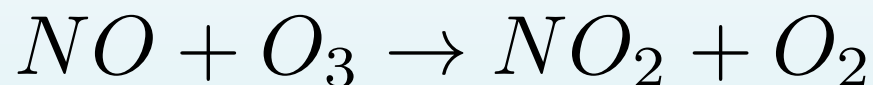
*Average distance between collisions*       $MFP = \frac{v}{\nu}$

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

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

## Bimolecular Reactions: Reaction Rate Coefficient

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

*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  $\rightarrow \sim 3.5 \times 10^{-10}$  for k*



# Bimolecular Reactions: Reaction Rate Coefficient

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- **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  $\exp(-\Delta E/T)$**