Kinetic Molecular Theory

Assumptions of the Kinetic Molecular Theory of gases:

1. No attractive forces between gas molecules.

2. Molecules' volumes are negligible compared to the volume of the gas sample as a whole.

3. Gas molecules are in constant, rapid, straight-line motion.

4. Collisions between molecules or the container walls are *elastic*; i.e., no loss of kinetic energy or momentum.

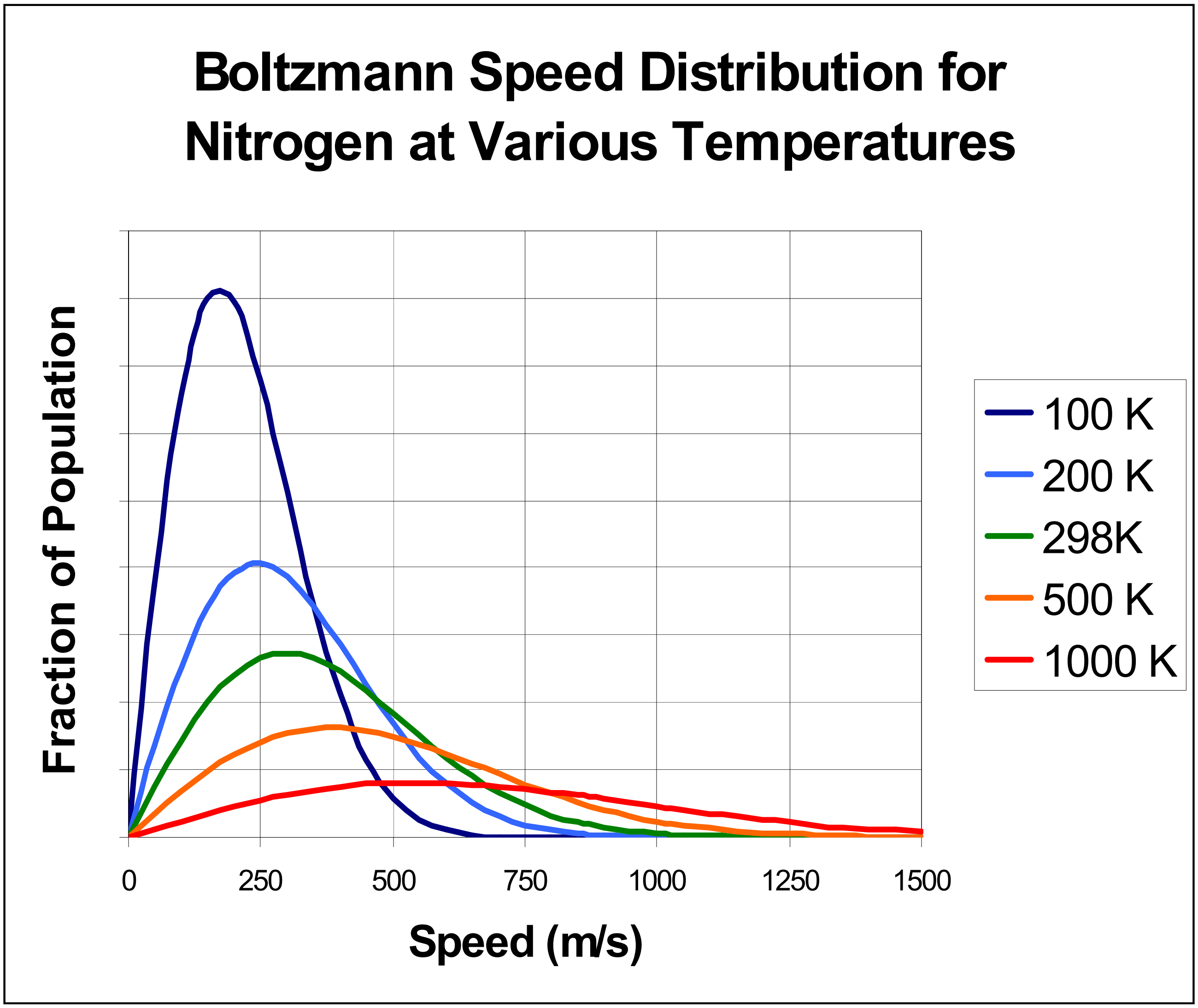
5. Gas pressure arises from molecules striking the walls of the container.

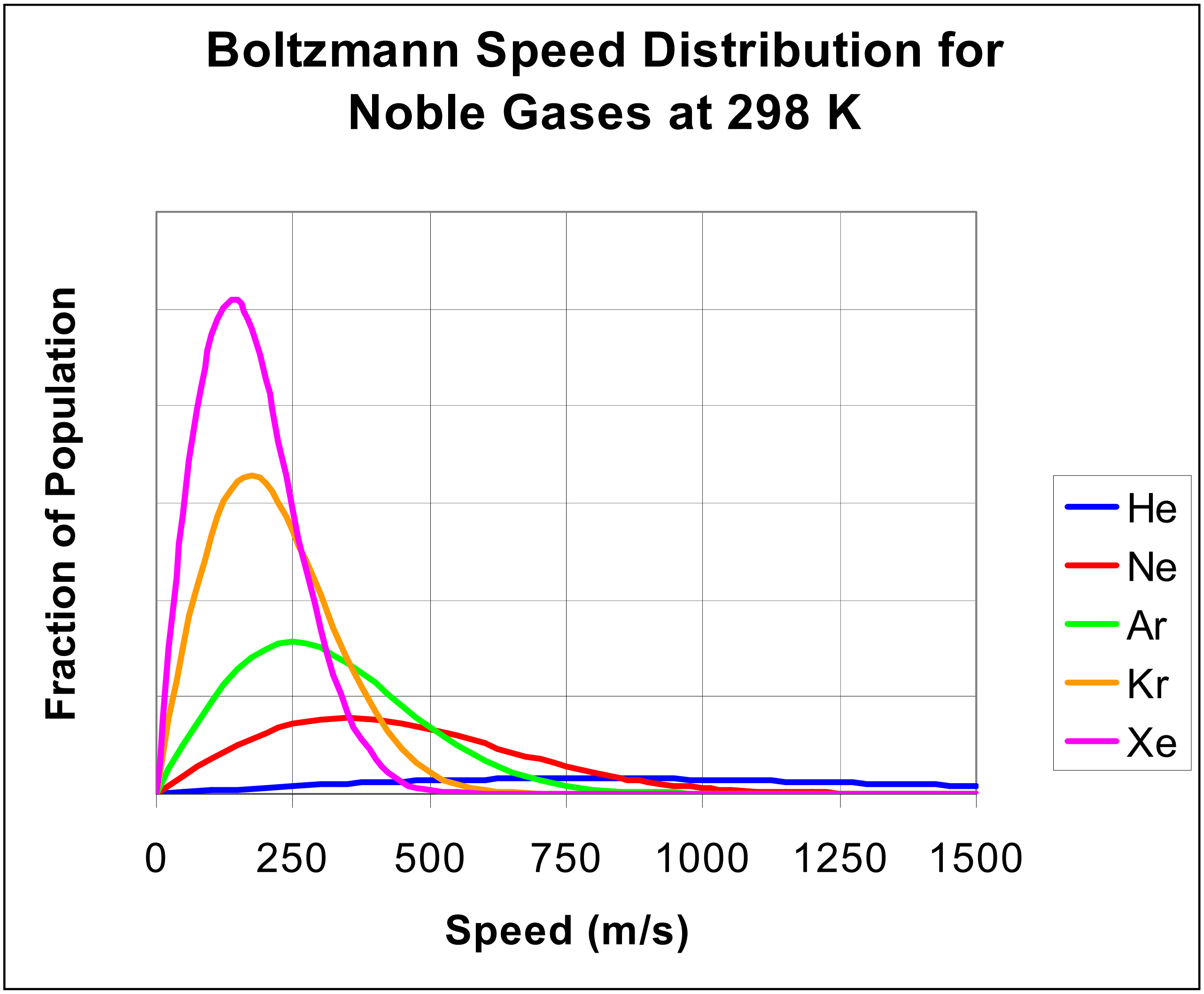
6. The average kinetic energy is proportional to the absolute temperature.

Molecular Velocities

☞ At any time, the molecules that make up the population in a sample have a wide range of individual velocities.

- Individual molecular velocities change as a result of collisions.
- Overall, velocities increase with temperature.
- At any temperature, heavy molecules move slower than light molecules.


Boltzmann Speed Distribution for Nitrogen at Various Temperatures
Fraction of Population
0
250
500
750
1000
1250
1500
Speed (m/s)
100 K
200 K
298K
500 K
1000 K



Boltzmann Speed Distribution for
Noble Gases at 298 K
Fraction of Population
0
250
500
750
1000
1250
1500
Speed (m/s)
He
Ne
Ar
Kr
Xe

Average and Root Mean Square Velocity

☞ The average velocity for a population of molecules would be

$$v_{\text{avg}} = \frac{\sum_{i=1}^{i=N} v_i}{N} = \frac{v_1 + v_2 + \ldots + v_N}{N}$$

☞ The root mean square velocity for a population of molecules is the square root of the sum of the individual molecular velocities squared divided by the number of molecules in the sample.

$$v_{\text{rms}} = \sqrt{\frac{\sum_{i=1}^{i=N} v_i^2}{N}} = \sqrt{\frac{v_1^2 + v_2^2 + \ldots + v_N^2}{N}}$$

- v_{rms} is the speed associated with the average kinetic energy of the population of molecules.

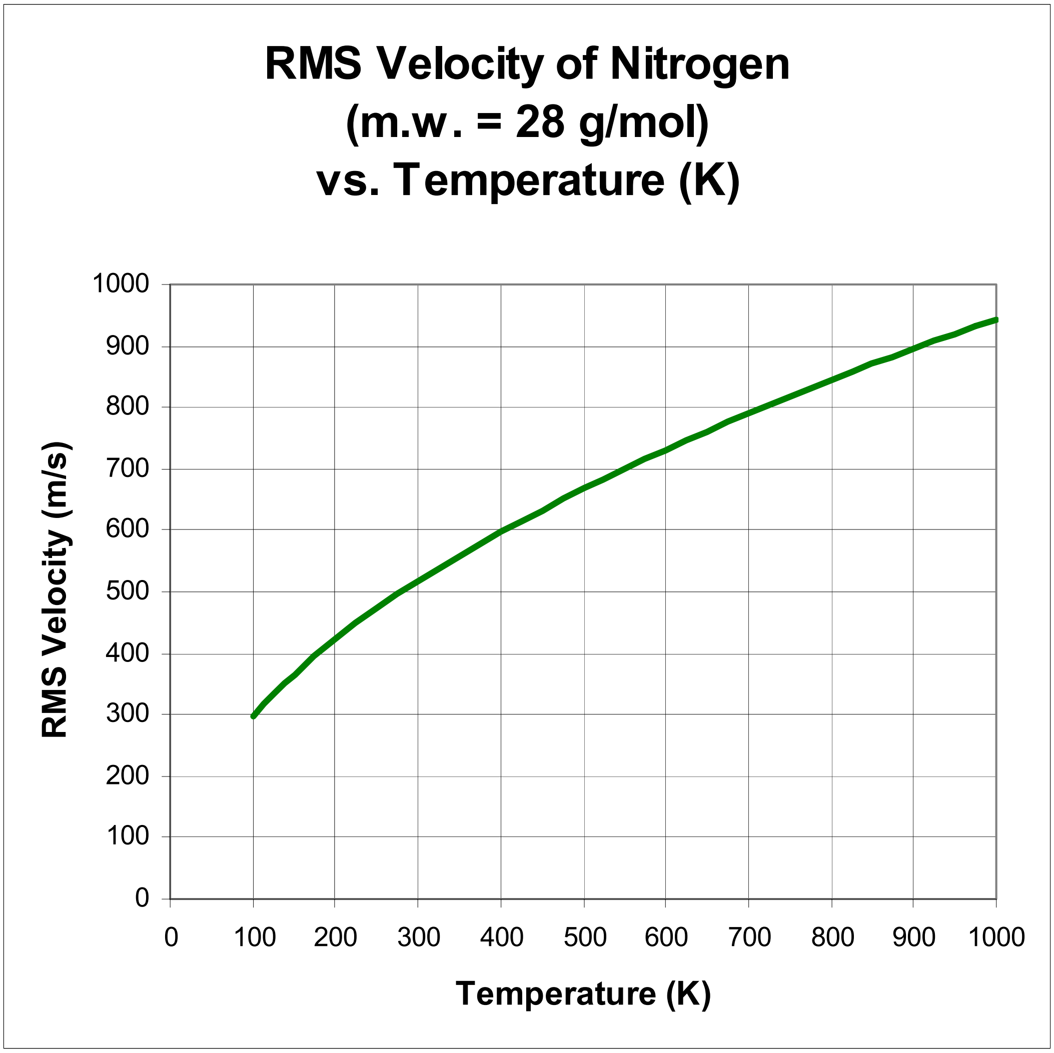
- The root mean squared velocity is not the same as the average velocity, but for an ideal gas $v_{\text{avg}} = 0.921\times v_{\text{rms}}$.

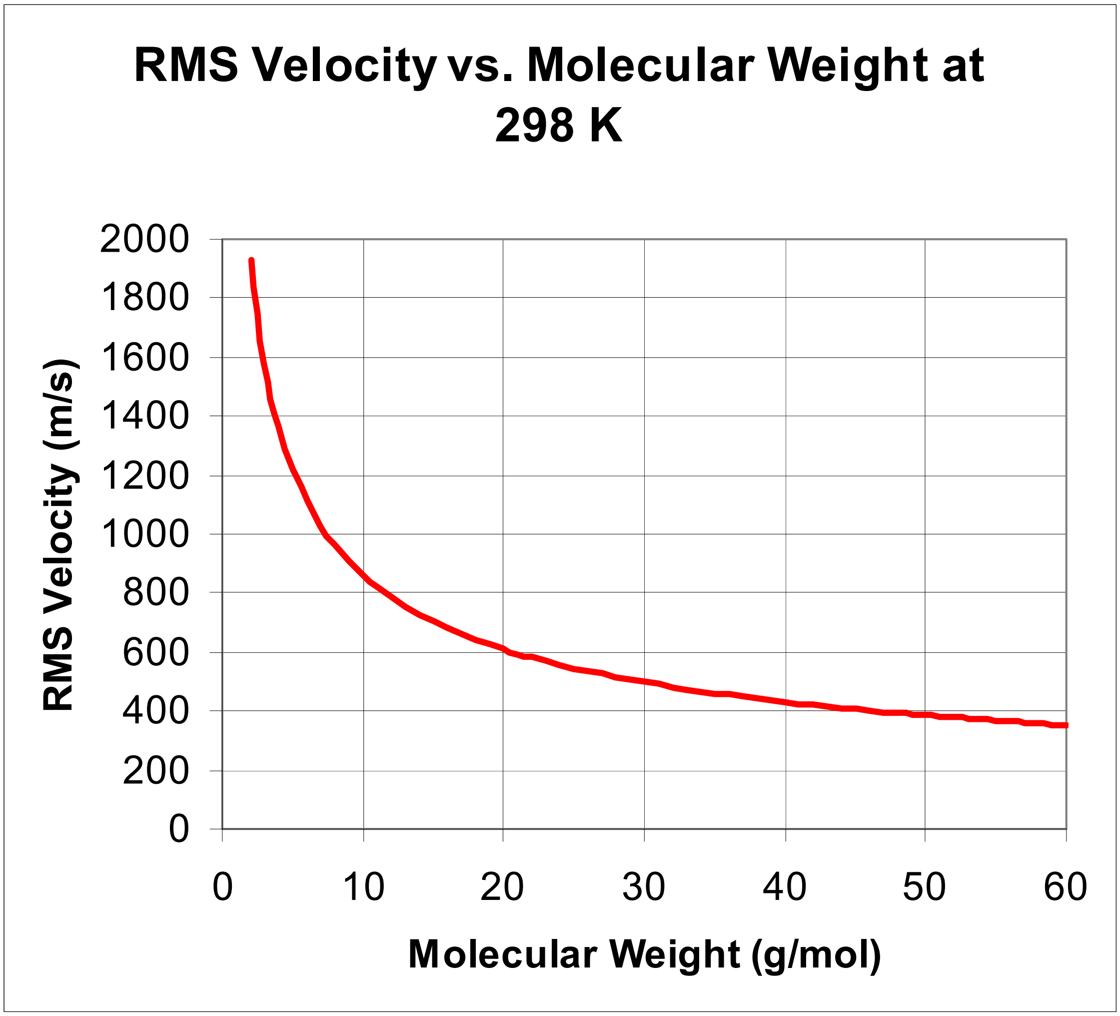
Root-Mean-Square Velocity for a Mole of Gas

☞ From Kinetic Molecular Theory, it can be shown that for one mole of ideal gas

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

where R = 8.3143 J/K·mol (gas constant in joules)
T = temperature in kelvin (K)
M = molecular weight in $kg \cdot mol^{-1}$


RMS Velocity of Nitrogen
(m.w. = 28 g/mol)
vs. Temperature (K)
RMS Velocity (m/s)
1000
900
800
700
600
500
400
300
200
100
0
0
100
200
300
400
500
600
700
800
900
1000
Temperature (K)


RMS Velocity vs. Molecular Weight at 298 K
RMS Velocity (m/s)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
Molecular Weight (g/mol)

Kinetic Energy of Gas Molecules

$$K = \frac{1}{2}mv^2$$

- For a particular gas, any velocity results in a corresponding kinetic energy.

- For a population of gas molecules, there will be a Boltzmann distribution of kinetic energies, just like the distribution of velocities.

Mean Kinetic Energy for a Mole of Gas

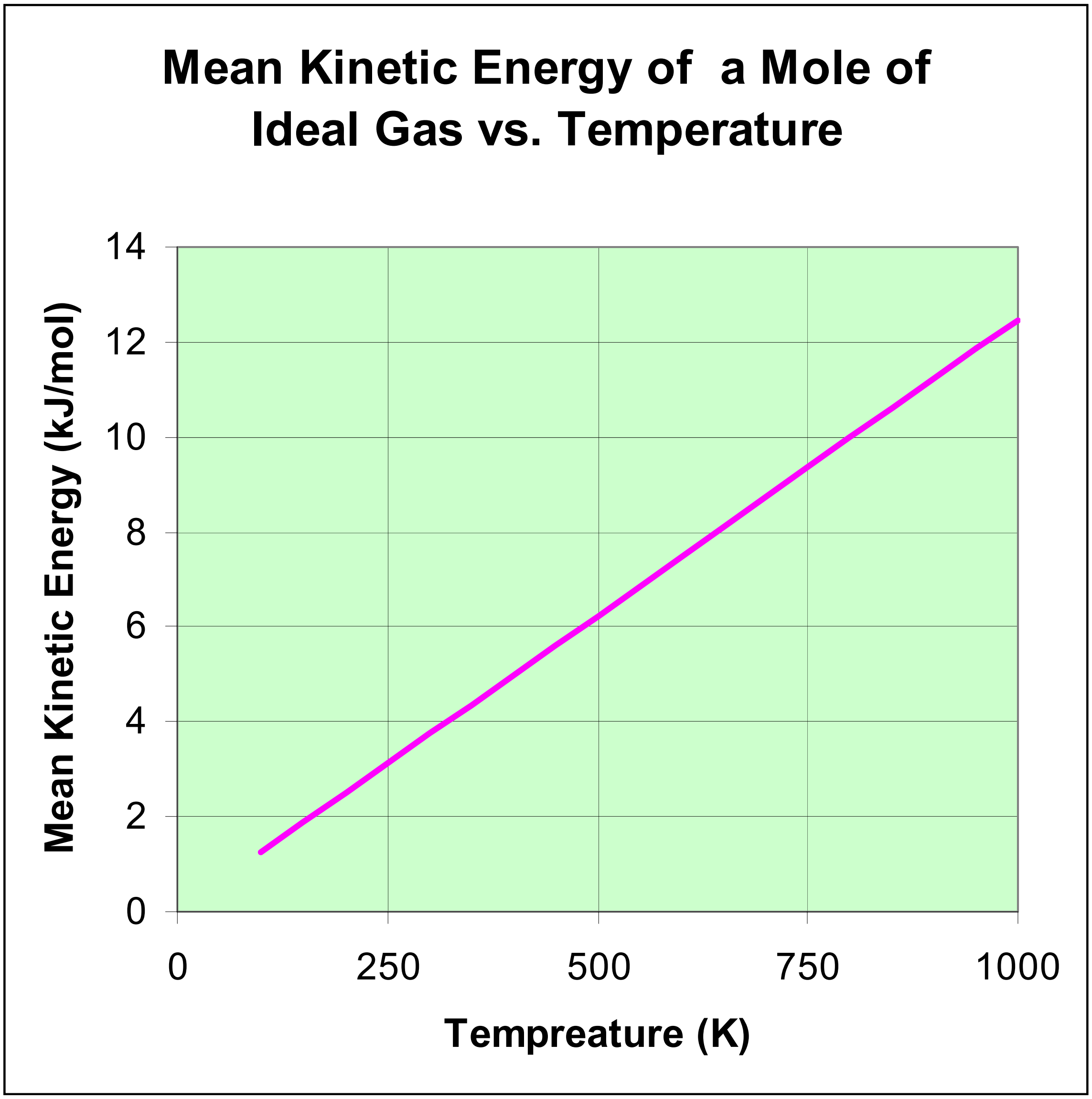
- For a mole of ideal gas, **mean kinetic energy, $\bar{K}$** is related to the root mean squared velocity, v_{rms}, by

$$\bar{K} = \tfrac{1}{2} M v_{rms}^2 = \tfrac{1}{2} M \left(\sqrt{\frac{3RT}{M}} \right)^2$$

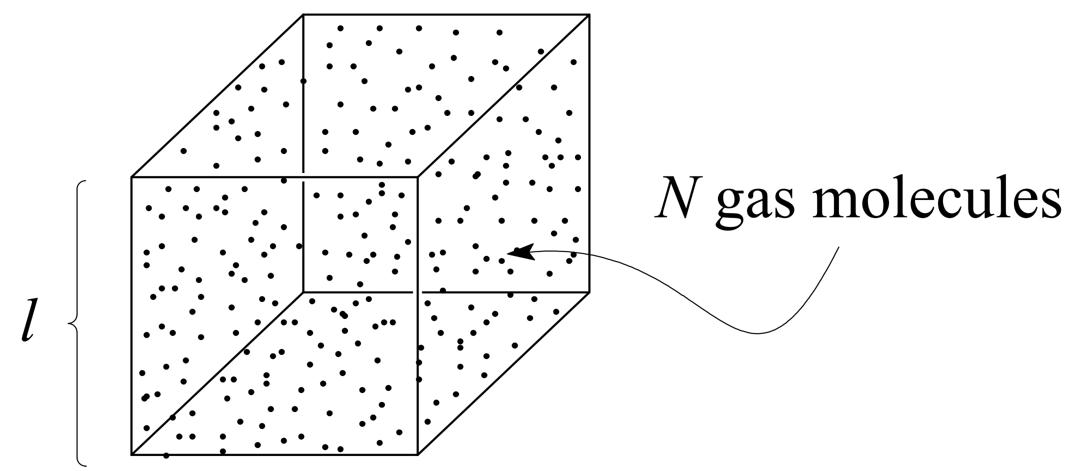
$$\bar{K} = \frac{3}{2} RT$$

  ☞ The mean kinetic energy of a sample of ideal gas is directly proportional to absolute temperature.

  ☞ The mean kinetic energy of a sample of ideal gas *does not* depend on the identity or molecular weight of the gas.


Mean Kinetic Energy of a Mole of
Ideal Gas vs. Temperature
Mean Kinetic Energy (kJ/mol)
14
12
10
8
6
4
2
0
0
250
500
750
1000
Tempreature (K)

Model for Deriving *PV = nRT* from Kinetic Molecular Theory



Kinetic Molecular Theory Derivation of $PV = nRT$

Pressure depends upon the following factors:

1. How hard the molecules hit the walls (*momentum* = *mv*)

$$\Rightarrow P \propto mv$$

2. How fast the molecules move (faster molecules make more collisions per second)

$$\Rightarrow P \propto v$$

3. Number of molecules (more molecules give more collisions)

$$\Rightarrow P \propto N \propto n$$

4. Distance between walls (larger l means fewer collisions per second)

$$\Rightarrow P \propto 1/l$$

5. Area of walls (larger area means fewer collisions per unit area)

$$\Rightarrow P \propto 1/l^2$$

Gathering all factors:

$$P \propto \frac{nmv^2}{l^3}$$

But kinetic energy is $K = ½mv^2$, so

$$P \propto \frac{nK}{l^3}$$

Kinetic molecular theory assumes that mean kinetic energy is proportional to absolute temperature ($K \propto T$), so

$$P \propto \frac{nT}{l^3}$$

The volume of the container is $V = l^3$, so

$$P \propto \frac{nT}{V}$$

To make an equation, use a proportionality constant (R):

$$P = \frac{nRT}{V} \quad \Rightarrow PV = nRT \qquad q.e.d.$$