Chemistry 1000 Lecture 18: The kinetic molecular theory of gases

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October 11, 2018

The kinetic molecular theory of gases

- Matter is in constant movement and, as we have seen, subject to a variety of intermolecular forces.
- Can we use basic ideas from physics to connect the microscopic forces acting on molecules to our everyday (macroscopic) world?
- Yes, if we take a statistical approach.
- This is made possible because of the very large size of Avogadro's number and with the help of the law of large numbers.
- In this context, the law of large numbers says that the behavior of a system containing many molecules is unlikely to deviate significantly from the statistical average of the properties of the individual molecules.

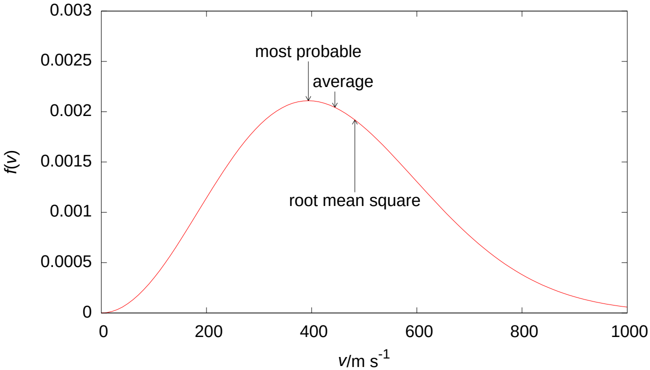
The Maxwell-Boltzmann distribution

- One of the results of the kinetic molecular theory is the Maxwell-Boltzmann distribution of molecular speeds.
- This is the probability distribution for the speeds (v) of molecules in a gas:

$$f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \exp\left(\frac{-Mv^2}{2RT}\right) v^2$$

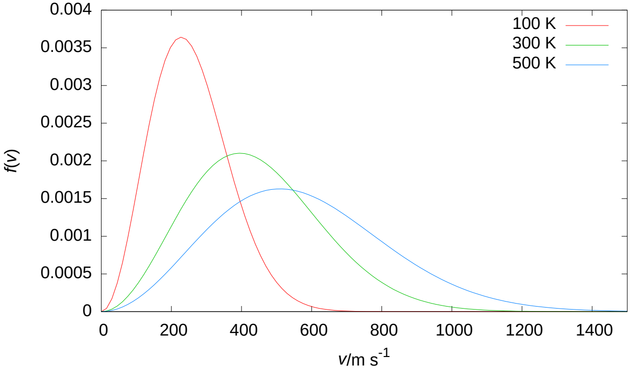
where M is the molar mass of an isotopomer, R is the ideal gas constant, and T is the absolute temperature.

Typical speeds and the Maxwell-Boltzmann distribution

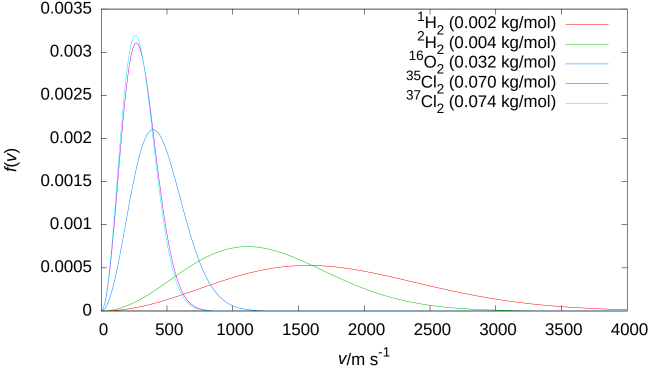


[$^{16}O_2$ at 298.15 K (25 °C)]

Maxwell-Boltzmann distribution for $^{16}O_2$ at different temperatures



Maxwell-Boltzmann distribution: Effect of mass



$[T = 300\,\mathrm{K}]$

Assumptions of the kinetic molecular theory for ideal gases

- The particles (molecules or atoms) of the gas are small compared to the average distance between them.

  Corollary: The particles occupy a negligible fraction of the volume.
- These particles are in constant motion.
- There are no intermolecular forces acting between them, except during collisions.
  - a good approximation for real gases provided the gas is at a sufficiently low pressure so that the distance between the molecules is *very* large.
- At constant temperature, the energy of the gas is constant.

Pressure of an ideal gas

Basic bits of physics we need:

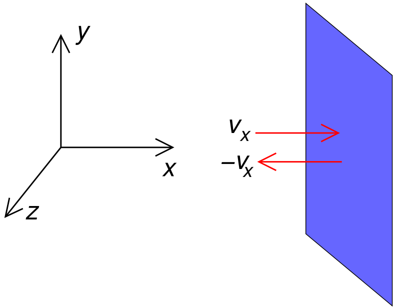
Pressure: $p = F/A$

Newton's second law: $F = ma = m\frac{\Delta v}{\Delta t}$

Newton's third law: For every action there is an equal and opposite reaction.

- The pressure on the wall of a container will be the force exerted on it due to collisions of molecules with the wall divided by the area of the wall.
- This force will be the negative of the sum of the average forces experienced by all the molecules.

- For simplicity, imagine a rectangular container containing an ideal gas.
- Consider a single particle impacting the wall:



- We choose the coordinate system so that the x axis is perpendicular to the wall.
- The y and z components of the velocity won't affect the pressure on this wall.
- If the total energy is conserved, then on average, the x component of the velocity after collision is just the negative of this component before collision.

- $\Delta v_x = v_{x,\text{after}} - v_{x,\text{before}} = -v_x - v_x = -2v_x$
- How often do collisions with this wall occur?
- If L_x is the x dimension of the container, then the particle travels $2L_x$ before returning, so the time between collisions is $\Delta t = 2L_x/v_x$.
- The average force experienced by one particle over time due to collisions with this wall is therefore

$$F_x = m\frac{\Delta v_x}{\Delta t} = -\frac{mv_x^2}{L_x}$$

- If $\overline{v_x^2}$ is the average value of v_x^2 for all the molecules in the gas, then the force on the wall is

$$F = \frac{Nm\overline{v_x^2}}{L_x}$$

where N is the total number of molecules of gas.

- The mean squared speed is

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

- There is no physical difference between the three directions in space, so $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$, from which we conclude that $\overline{v_x^2} = \frac{1}{3}\overline{v^2}$.

$$F = \frac{Nm\overline{v^2}}{3L_x}$$

- $p = F/A$, so

$$p = \frac{Nm\overline{v^2}}{3AL_x} = \frac{Nm\overline{v^2}}{3V}$$

using the fact that the area of the wall times the distance between the walls is the volume of the container.

$$pV = \frac{1}{3}Nm\overline{v^2}$$

Root mean squared speed and temperature

$$pV = \frac{1}{3} N m \overline{v^2}$$

- In this equation, m is the mass of one molecule and N is the number of molecules.
- We have $N = nN_A$ and $m = M/N_A$.

$$\therefore pV = \frac{1}{3} n M \overline{v^2}$$

- Experimentally, we know that $pV = nRT$ for dilute (ideal) gases. Combining the two, we get

$$\frac{1}{3} M \overline{v^2} = RT \implies \overline{v^2} = \frac{3RT}{M} \implies \boxed{\sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}}}$$

- $\sqrt{\overline{v^2}}$ is the root mean squared (rms) speed.

Example: rms speed of N_2

- The calculation of rms speeds is straightforward, provided we use SI units consistently.
- The SI unit of mass is the kg.
- For N_2, $M = 2(14.0067 \times 10^{-3}\,\text{kg/mol}) = 2.801\,34 \times 10^{-2}\,\text{kg/mol}$.
- At room temperature, we would have

$$\begin{aligned}\sqrt{\overline{v^2}} &= \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314\,472\,\text{J}\,\text{K}^{-1}\text{mol}^{-1})(293\,\text{K})}{2.801\,34 \times 10^{-2}\,\text{kg/mol}}} \\ &= 511\,\text{m/s}\end{aligned}$$

The Boltzmann constant

- Recall the ideal gas equation

$$pV = nRT$$

- If we want to rewrite the ideal gas equation in terms of the number of molecules (rather than the number of moles of molecules), we use $n = N/N_A$:

$$pV = (N/N_A)RT = N(R/N_A)T$$

- $R/N_A \equiv k_B$ is Boltzmann's constant.
  It is the ideal gas constant on a per molecule basis.

$$pV = Nk_BT$$

$$k_B = 1.380\,649 \times 10^{-23}\,\mathrm{J\,K^{-1}}$$

Average kinetic energy

$$pV = \frac{1}{3}Nm\overline{v^2}$$

- The average kinetic energy is $K = \frac{1}{2}m\overline{v^2}$, so

$$pV = \frac{2}{3}NK$$

- Since $pV = Nk_BT$, equating the two expressions for pV gives

$$\boxed{K = \tfrac{3}{2}k_BT}$$

Why and when the ideal gas law breaks down

- Not all gases behave ideally under all conditions.
- Intermolecular forces can be significant.
- The volume taken up by the molecules can be a significant fraction of the total volume of the container.
- Both of these effects become more important as the density of the gas increases.
- The density is proportional to

$$\frac{n}{V} = \frac{p}{RT}$$

so nonideal effects should become important at high pressures or at low temperatures.

Excluded volume

- The molecules occupy some of the volume of the container.
- The volume available for them to move in is therefore less than the total volume of the container.
- We can correct for this by subtracting the excluded volume, which will be proportional to the number of molecules, from the total volume in the ideal gas law:

$$p(V - nb) = nRT$$

- b is a constant determined experimentally and is about four times the volume of a molecule times Avogadro's constant.

Intermolecular forces

- Provided the density isn't too high, intermolecular forces are primarily attractive, as discussed in a previous lecture.
- Attractive forces will tend to decrease the pressure:
  As a molecule approaches the container wall, there is an imbalance between the number of molecules ahead of it and the number behind. The force of attraction from molecules behind provide a braking force which slows the approach of a molecule to the wall, and thus decreases the force of impact.

- The attractive force is found to depend on the square of the density.
- Including this correction in the equation of state for a gas would give

$$\left(p + \frac{an^2}{V^2}\right) V = nRT$$

where a is a constant determined experimentally that depends on the strength of the intermolecular forces, and thus on the particular gas we are studying.

van der Waals equation

- Putting both corrections together, we get the van der Waals equation:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

- Solving the vdW equation for p isn't too difficult:

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Example

For N_2, $a = 0.1408\,\text{Pa}\,\text{m}^6\text{mol}^{-2}$ and $b = 3.91 \times 10^{-5}\,\text{m}^3/\text{mol}$.
If we have 40 mol of N_2 in $1.0\,\text{m}^3$ at 298 K, then

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$p = \frac{(40\,\text{mol})(8.314\,472\,\text{J}\,\text{K}^{-1}\text{mol}^{-1})(298\,\text{K})}{1.0\,\text{m}^3 - (40\,\text{mol})(3.91 \times 10^{-5}\,\text{m}^3/\text{mol})} - \frac{(0.1408\,\text{Pa}\,\text{m}^6\text{mol}^{-2})(40\,\text{mol})^2}{(1.0\,\text{m}^3)^2}$$

$$= \frac{(40\,\text{mol})(8.314\,472\,\text{J}\,\text{K}^{-1}\text{mol}^{-1})(298\,\text{K})}{0.9984\,\text{m}^3} - \frac{(0.1408\,\text{Pa}\,\text{m}^6\text{mol}^{-2})(40\,\text{mol})^2}{(1.0\,\text{m}^3)^2}$$

$$= 99\,264 - 225\,\text{Pa} = 99\,\text{kPa}$$

Example

Suppose we have 4000 mol of N_2 in $1.0\,\text{m}^3$ at 298 K:

$$p = \frac{(4000\,\text{mol})(8.314\,472\,\text{J}\,\text{K}^{-1}\text{mol}^{-1})(298\,\text{K})}{1.0\,\text{m}^3 - (4000\,\text{mol})(3.91\times10^{-5}\,\text{m}^3/\text{mol})} - \frac{(0.1408\,\text{Pa}\,\text{m}^6\text{mol}^{-2})(4000\,\text{mol})^2}{(1.0\,\text{m}^3)^2}$$

$$= \frac{(4000\,\text{mol})(8.314\,472\,\text{J}\,\text{K}^{-1}\text{mol}^{-1})(298\,\text{K})}{0.8436\,\text{m}^3} - \frac{(0.1408\,\text{Pa}\,\text{m}^6\text{mol}^{-2})(4000\,\text{mol})^2}{(1.0\,\text{m}^3)^2}$$

$$= 1.175\times10^7 - 2.25\times10^6\,\text{Pa} = 9.5\,\text{MPa}$$

- Using the ideal gas law, we would have predicted 9.9 MPa.