

Chapter 21 – Kinetic Theory of Gases

This chapter examines the behavior of an ideal gas from a molecular point of view. It shows how the macroscopic behavior of a gas - described in terms of pressure, volume, temperature - can be related to the statistical average of the microscopic motions.

Assume that we have a container of an ideal gas with the following properties:

- Large number of molecules with average spacing between molecules large compared with the size of the molecules.
- Molecules obey Newton's laws of motion.
- Molecules collide elastically with each other and with the walls of the container.
- Forces between molecules are short range – only important during collisions.
- Container consists of only one type of gas (not a mixture).

The pressure exerted by the gas on the walls of the container is a result of collisions by the molecules. Consider a cubical container with dimensions $d \times d \times d$. A molecule with a component of velocity in the x -direction will collide with a wall perpendicular to the x -axis and transfer an amount of momentum to the wall given by

$$\Delta p = 2mv_x$$

The average time between collisions with this wall is

$$\Delta t = 2d / v_x$$

The average force exerted on the wall by this collision is

$$F_1 = \frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2d / v_x} = \frac{mv_x^2}{d}$$

For N molecules making collisions, the total average force is

$$F = \frac{Nmv_x^2}{d}$$

where $\overline{v_x^2}$ is the average of the square of the velocity in the x -direction. However, because of the random motion

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

and

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}, \text{ or } \overline{v_x^2} = \frac{1}{3}\overline{v^2}$$

Thus,

$$F = \frac{N m \overline{v^2}}{3d}$$

The pressure exerted on the wall is

$$P = \frac{F}{A} = \frac{F}{d^2} = \frac{N m \overline{v^2}}{3d^3} = \frac{N m \overline{v^2}}{3V}$$

Or,

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

We compare this with the ideal gas equation, which is

$$PV = nRT = N k_B T \quad (\text{where } k_B = nR/N = R/N_A)$$

This means that the average translational kinetic energy is related to the temperature as

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T$$

The total translational kinetic energy in the gas is

$$E = N \frac{1}{2} m \overline{v^2} = \frac{3}{2} N k_B T = \frac{3}{2} nRT$$

From the above we can determine the root-mean-square (rms) speed of the molecules as

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}$$

We can also write this as

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

where M is the molar mass, since $M = N_A m$ and $N_A k_B = R$.

Example:

What is the rms speed of nitrogen molecules at 20°C? For N_2 , $M = 28 \text{ g/mole} = 0.028 \text{ kg/mole}$.

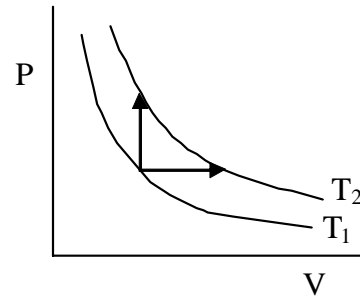
$$v_{rms} = \sqrt{\frac{3(8.31 \text{ J/mole} \cdot \text{K})(293 \text{ K})}{(0.028 \text{ kg/mole})}} = \underline{511 \text{ m/s}}$$

What is the total translational kinetic energy in 1 mole of the gas?

$$E = N \frac{1}{2} m \overline{v^2} = N \frac{3}{2} k_B T = \frac{3}{2} nRT = \frac{3}{2} (1 \text{ mole}) (8.31 \text{ J/mole} \cdot \text{K}) (293 \text{ K}) = \underline{3.65 \times 10^3 \text{ J}}$$

Specific Heat of an Ideal Gas

For gases, it is conventional to refer to the *molar* specific heat, which is the heat absorbed per *mole* per unit temperature rise. The molar specific heat, and thus the heat absorbed for a given temperature rise, depends on whether the pressure or the volume is held constant as the temperature increases.



$$Q = nc_v \Delta T \quad (\text{constant volume})$$

$$Q = nc_p \Delta T \quad (\text{constant pressure})$$

From the 1st law of thermodynamics, no work is done in a constant volume process. Thus,

$$\Delta U = Q \quad (\text{constant volume})$$

For a *monatomic* gas the internal energy is the total translational kinetic energy. Then

$$U = E = \frac{3}{2} nRT, \quad \Delta U = \frac{3}{2} nR \Delta T, \quad \text{and}$$

$$\frac{3}{2} nR \Delta T = nc_v \Delta T, \quad \text{or}$$

$$c_v = \frac{3}{2} nR$$

For a constant pressure process, $\Delta W = -P\Delta V = -nR\Delta T$. So,

$$\Delta U = Q + W = Q - P\Delta V = Q - nR\Delta T,$$

or

$$Q = \Delta U + nR\Delta T = \frac{3}{2}nR\Delta T + nR\Delta T = \frac{5}{2}nR\Delta T.$$

Then,

$$c_p = \frac{Q}{n\Delta T} = \frac{5}{2}nR$$

and

$$c_p = c_v + R$$

During a constant volume process, no work is done so all the heat absorbed goes into increasing the internal energy and the temperature. During a constant pressure process, the gas expands and reduces the internal energy by doing work. Thus, more heat can be absorbed for a given temperature change.

Specific Heat of Diatomic Gases

Previously, it was shown that

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$$

Since $\frac{1}{2}m\overline{v^2} = \frac{1}{2}m\overline{v_x^2} + \frac{1}{2}m\overline{v_y^2} + \frac{1}{2}m\overline{v_z^2}$, this means that the average kinetic energy is

$\frac{1}{2}k_B T$ per term or per degree of freedom. A diatomic molecule is somewhat like two masses connected by a spring. The molecule can rotate about its center of mass and the atoms can vibrate back and forth along the line connecting them. Since the rotational inertia about an axis connecting the atoms is extremely small, there are two energy terms corresponding to rotation about the other two perpendicular axes (two degrees of freedom). The average kinetic energy of each of these terms is $\frac{1}{2}k_B T$ and the total average rotational energy is $k_B T$.

The vibrational energy of the mass-spring system consists of a kinetic energy and a potential energy term (also two degrees of freedom). Each of these terms has an average of $\frac{1}{2}k_B T$ and the total average vibrational energy is $k_B T$.

Because of these additional degrees of freedom, the specific heat of a diatomic molecule is greater than that of a monatomic molecule ($\frac{1}{2}R$ for each degree of freedom). The

rotational and vibrational energies of a molecule are quantized. That is, only certain discrete energies are allowed. In order to excite these rotational and vibrational levels, the gas must be at a sufficiently high temperature. At low temperatures, only translational motions can occur. At higher temperatures, the molecular collisions are sufficient to excite the rotational levels. At still higher temperatures, the vibrational energy levels can be excited. Thus, the specific heat of a diatomic molecule will increase with temperature, giving evidence of the quantum nature of the energies.