4.14: Collisions between like Gas Molecules

When we consider collisions between different gas molecules of the same substance, we can denote the relative velocity and the expected value of the relative velocity as v_{11} and $\langle v_{11} \rangle$, respectively. By the argument we make above, we can find the number of collisions between any one of these molecules and all of the others. Letting this collision frequency be $\tilde{\nu}_{11}$, we find

$$\tilde{\nu}_{11} = N_1 \pi \sigma_{11}^2 \left\langle v_{11} \right\rangle,$$

where $\sigma_{11} = 2\sigma_1$. Since we have

$$\left\langle v_{11} \right\rangle = \sqrt{2} \left\langle v_1 \right\rangle,$$

while

$$\left\langle v_1 \right\rangle = \sqrt{8kT/\pi m_1},$$

we have $\left\langle v_{11} \right\rangle = 4\sqrt{kT/\pi m_1}$. The frequency of collisions between molecules of the same substance becomes

$$\tilde{\nu}_{11} = N_1 \pi \sigma_{11}^2 \left\langle v_{11} \right\rangle = 4 N_1 \sigma_{11}^2 \left(\frac{\pi kT}{m_1} \right)^{1/2}$$

The mean time between collisions, τ_{11}, is

$$\tau_{11} = 1/\tilde{\nu}_{11}$$

and the mean free path, λ_{11},

$$\lambda_{11} = \left\langle v_1 \right\rangle \tau_{11} = \frac{1}{\sqrt{2} N_{\ 1}} \pi \sigma_{11}^2$$

When we consider the rate of collisions between all of the molecules of type 1 in a container, ρ_{11}, there is a minor complication. If we multiply the collision frequency per molecule, $\tilde{\nu}_{11}$, by the number of molecules available to undergo such collisions, N_1, we count each collision twice, because each such collision involves two type 1 molecules. To find the collision rate among like molecules, we must divide this product by 2. That is,

$$\rho_{11} = \frac{N_1 \tilde{\nu}_{11}}{2} = 2 N_1^2 \sigma_{11}^2 \left(\frac{\pi kT}{m_1} \right)^{1/2}$$