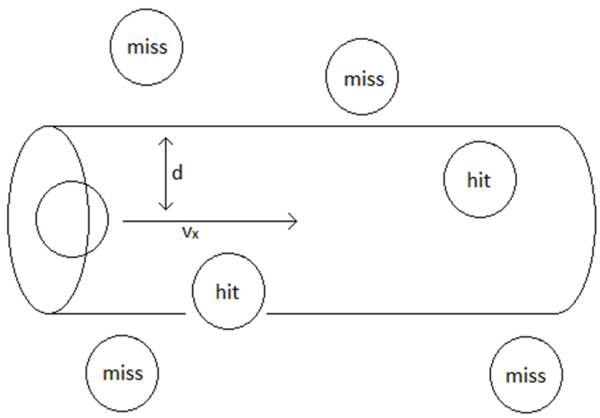
9.14: Collisions with Other Molecules

A major concern in the design of many experiments is collisions of gas molecules with other molecules in the gas phase. For example, molecular beam experiments are often dependent on a lack of molecular collisions in the beam that could degrade the nature of the molecules in the beam through chemical reactions or simply being knocked out of the beam.

In order to predict the frequency of molecular collisions, it is useful to first define the conditions under which collisions will occur. For convenience, consider all of the molecules to be spherical and in fixed in position except for one which is allowed to move through a “sea” of other molecules. A molecular collision will occur every time the center of the moving molecule comes within one molecular diameter of the center of another molecule.



One can easily determine the number of molecules the moving molecule will “hit” by determining the number of molecules that lie within the “collision cylinder”. Because we fixed the positions of all but one of the molecules, we must use the relative speed of the moving molecule, which will be given by

$$v_{rel} = \sqrt{2} \times v$$

The volume of the collision cylinder is given by

$$V_{col} = \sqrt{2}\, v\, \Delta t\, A$$

The **collisional cross section**, which determined by the size of the molecule is given by

$$\sigma = \pi d^2$$

Some values of σ are given in the table below:

Table 2.6.1: Collisional cross-section of Select Species

Molecule	σ (nm^2)
He	0.21
Ne	0.24
N_2	0.43
CO_2	0.52
C_2H_4	0.64

Since the number of molecules within the collision cylinder is given by

$$N_{col} = \frac{N}{V} V_{col}$$

and since the number density (N/V) is given by

$$\frac{N}{V} = \frac{p}{k_B T}$$

the number of collisions is given by

$$N_{col} = \frac{p}{k_B T}(\sqrt{2}\, v \Delta t \sigma)$$

The frequency of collisions (number of collisions per unit time) is then given by

$$Z = \frac{\sqrt{2} p \sigma}{k_B T} \langle v \rangle$$

Perhaps a more useful value is the **mean free path** (λ), which is the distance a molecule can travel on average before it collides with another molecule. This is easily derived from the collision frequency. How far something can travel between collisions is given by the ratio of how fast it is traveling and how often it hits other molecules:

$$\lambda = \frac{\langle v \rangle}{Z}$$

Thus, the mean free path is given by

$$\lambda = \frac{k_B T}{\sqrt{2} p \sigma}$$

The mere fact that molecules undergo collisions represents a deviation from the kinetic molecular theory. For example, if molecules were infinitesimally small ($\sigma \approx 0$) then the mean free path would be infinitely long! The finite size of molecules represents one significant deviation from ideality. Another important deviation stems from the fact that molecules do exhibit attractive and repulsive forces between one another. These forces depend on a number of parameters, such as the distance between molecules and the temperature (or average kinetic energy of the molecules.)