CEN 207 Physical Chemistry

Text book:

Atkins' Physical Chemistry, Peter Atkins, Julio de Paula, James Keeler, 11th Edition, Oxford University Press.

Reference books

. Physical Chemistry, Robert J. Silbey, Robert A. Alberty, Moungi G. Bawendi

. Physical Chemistry, Ira N. Levine

B. The kinetic model

Mean values

To calculate the mean value of any power of the speed by evaluating the appropriate integral.

$$F(v_1, v_2) = \int_{v_1}^{v_2} f(v)\,dv$$

The average value of v^n is calculated as

$\langle v^n \rangle = \int_0^\infty v^n f(v)\,dv$ for n=2 $\qquad \langle v^2 \rangle = \frac{3RT}{M}$ Mean square speed (KMT)

It follows that the root-mean-square speed of the molecules of the gas is

$$v_{rms} = \langle v^2 \rangle = \left(\frac{3RT}{M}\right)^{1/2}$$

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B. The kinetic model

Mean values

The Maxwell-Boltzmann distribution can be used to evaluate the mean speed (v_{mean}) of the molecules in a gas:

$$v_{mean} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8}{3\pi}\right)^{1/2} v_{rms}$$ mean speed (KMT)

$$v_{mp} = \left(\frac{2RT}{M}\right)^{1/2} = \left(\frac{2}{3}\right)^{1/2} v_{rms}$$ most probable speed (KMT)

B. The kinetic model

Mean values

The mean relative speed (v_{rel}) the mean speed with which one molecule approaches another of the same kind, can also be calculated from the distribution:

$$v_{rel} = 2^{1/2} v_{mean}$$

mean relative speed (KMT, identical molecules)

For the relative mean speed of two dissimilar molecules of masses m_A and m_B:

$$v_{rel} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \rightarrow \mu = \frac{m_A m_B}{m_A + m_B}$$

mean relative speed (perfect gas)

B. The kinetic model

Collisions

The collision frequency:
The kinetic model can be used to deduce the collision frequency, z,

$z = \sigma v_{rel} \mathcal{N}$ **Collison frequency** (KMT)

$\mathcal{N} = N/V$ V: the volume of the tube; N: the total number of molecules

The parameter σ is called the **collision cross-section** of the molecules.
In terms of pressure for the perfect gas equation $R=N_a k$

$$\frac{N}{V} = \frac{nN_A}{V} = \frac{nN_A}{nRT/p} = \frac{pN_A}{RT} = \frac{p}{kT}$$

Then

$$z = \frac{\sigma v_{rel} p}{kT}$$

Collison frequency (KMT)

B. The kinetic model

The mean free path

The mean free path (λ) is the average distance a molecule travels between collisions. If a molecule collides with a frequency **z**, it spends a time **1/z** in free flight between collisions, and therefore travels a distance **(1/z)v$_{rel}$**. It follows that the mean free path is

$$\lambda = \frac{v_{rel}}{z}$$

Mean free path (KMT)

$$z = \frac{\sigma v_{rel} p}{kT}$$

$$\lambda = \frac{v_{rel}}{z} = \frac{kT}{\sigma p}$$

Mean free path (perfect gas)