Physical Chemistry

Lecture 1

Distributions and averages

Characteristics of macroscopic materials

- Large numbers of particles, N
- Distribution of properties: $F(v) = n(v)/N$
  - Example: speed
  - Describe with a distribution function, $F(v)$
    - Normalized: $\int_0^\infty F(v)dv = 1$
    - Average of a function of speed

$$< f(v) > = \int_0^\infty F(v) f(v) dv$$

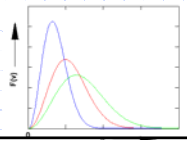
Boltzmann's distribution

- Speed distribution function at dynamic equilibrium
- Consider only kinetic energy

$$F(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right)$$

- This is normalized

$$\int_0^\infty F(v)dv = 1$$



Calculating average molecular properties

- Use the distribution function

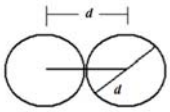
$$< f(v) > = \int_0^\infty f(v) F(v) dv$$

- Example: average speed

$$< v > = \int_0^\infty v F(v) dv = \sqrt{\frac{8kT}{\pi m}}$$

Molecular collisions

- Collisions dominate effects that depend on close proximity of molecules
- "Hard-sphere" model

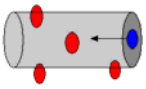


Collisions of a molecule

- Determined by the number of molecules in the space ($N = n^* V$)
- Collision frequency

$$< z_{AA} > = n^* \pi d^2 < v_{rel} >$$

$$= \sqrt{2}\, n^* \pi d^2 < v >$$



- Mean-free path

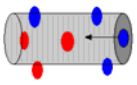
$$\lambda = \frac{< v >}{< z_{AA} >} = \frac{1}{\sqrt{2}\,\pi d^2 n^*} = \frac{kT}{\sqrt{2}\,P\pi d^2}$$

Collisions of unlike molecules

- Three different kinds of collision
- Collision frequencies per molecule

$$< z_{AA} > = n_A^* \pi d^2 < v_{rel} >$$

$$= \sqrt{2}\, n_A^* \pi d^2 < v >$$



$$< z_{A:B} > = \pi d_{AB}^2 < v_{AB} > n_B^*$$

$$< z_{B:A} > = \pi d_{AB}^2 < v_{AB} > n_A^*$$

$$d_{AB} = \frac{d_A + d_B}{2}$$

Total collisions in a mixture

- Often must know the total number of collisions per unit time

$$Z_{AA} = < z_{AA} > \frac{n_A^*}{2} = \frac{\pi d_A^2 < v_A >}{\sqrt{2}} n_A^{*2}$$

$$Z_{AB} = < z_{A:B} > n_A^* = \pi d_{AB}^2 < v_{AB} > n_A^* n_B^*$$

$$Z_{AB} = < z_{B:A} > n_B^* = \pi d_{AB}^2 < v_{AB} > n_A^* n_B^*$$

Summary

- Simple kinetic theory allows calculation of various average properties
- Calculate average properties with the distribution function
- Collision frequency important for properties that depend on the molecules being in close proximity
- Mixtures have multiple kinds of collisions