Physical Chemistry (Chem 132A)

Lecture 18
Wednesday, November 15

Homework #7 is due November 18

Schedule

1. **Homework 7 is due on Saturday, November 18.**
   This will probably be the last homework assignment before the second midterm.

2. **Second Midterm exam: Wednesday, November 22**
   second midterm will cover Chapters 1—6, 19

   - **there will be a seating chart**
   - **same procedures as midterm 1**
     1 page notes allowed
     bring calculator

How do Reactions Occur?

A + B ➔ C

Collisions!!

Foundations: B.3 –The Boltzmann Distribution

Chapter 1B: molecular speed distributions and collisions

pgs. 37--43

The Boltzmann Distribution

$$\frac{N_j}{N_i} = e^{-\frac{(\varepsilon_j - \varepsilon_i)}{kT}}$$

ε is energy per molecule
k is Boltzmann's constant

$$\frac{N_j}{N_i} = e^{-\frac{(E_j - E_i)}{RT}}$$

E is energy per mole
R is gas constant = N_Ak

Distribution of Molecular Speeds

$$\varepsilon = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

Kinetic energy of molecule

f(v)dv = fraction of molecules with speed in the range v to v + dv

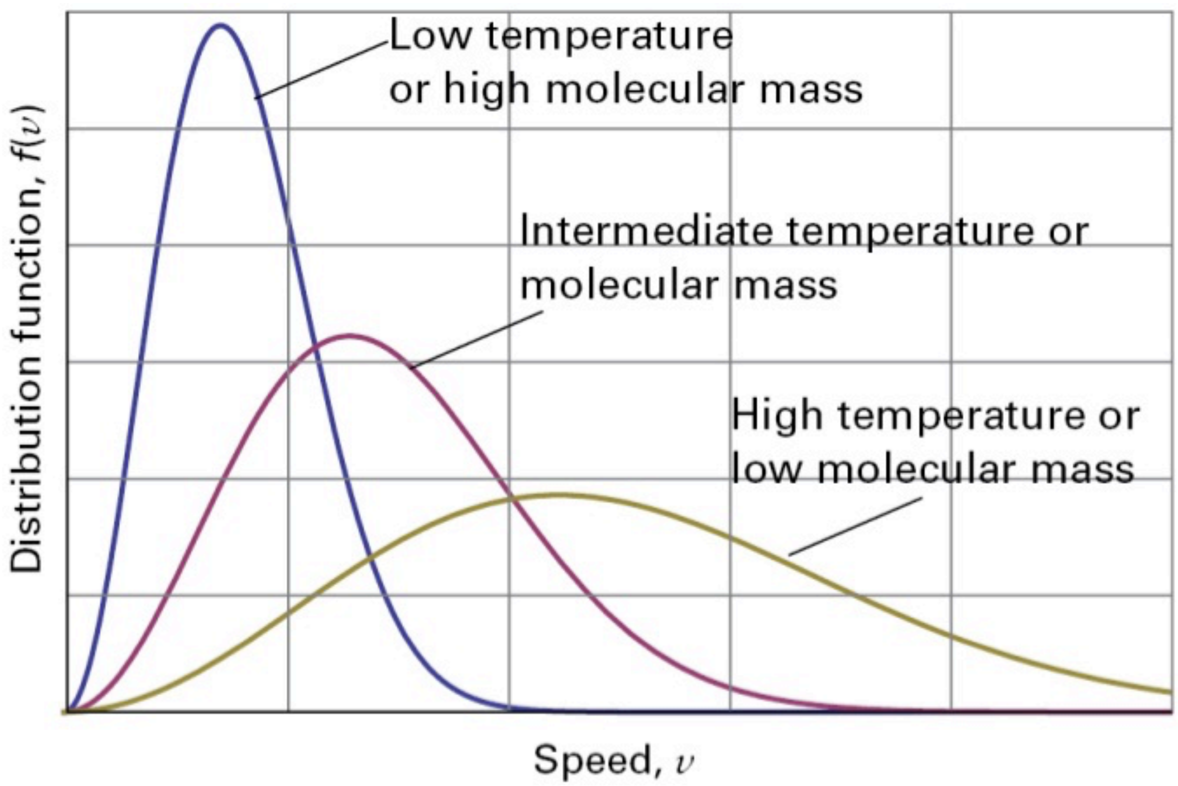
$$f(v) = Ke^{-\left(\frac{1}{2}mv_x^2+\frac{1}{2}mv_y^2+\frac{1}{2}mv_z^2\right)} = Ke^{-\left(\frac{1}{2}mv_x^2\right)}e^{-\left(\frac{1}{2}mv_y^2\right)}e^{-\left(\frac{1}{2}mv_z^2\right)} = f(v_x)f(v_y)f(v_z)$$

$$\int_{-\infty}^{+\infty} f(v_x)\,dv_x = 1$$

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

This can also be written in terms of M and R

Properties of the Boltzmann Speed Distribution



Calculation of Averages

$$\left\langle v^n \right\rangle = \int_0^\infty v^n f\left(v\right) dv$$

$$v_{mean} = \int_0^\infty v f\left(v\right) dv = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

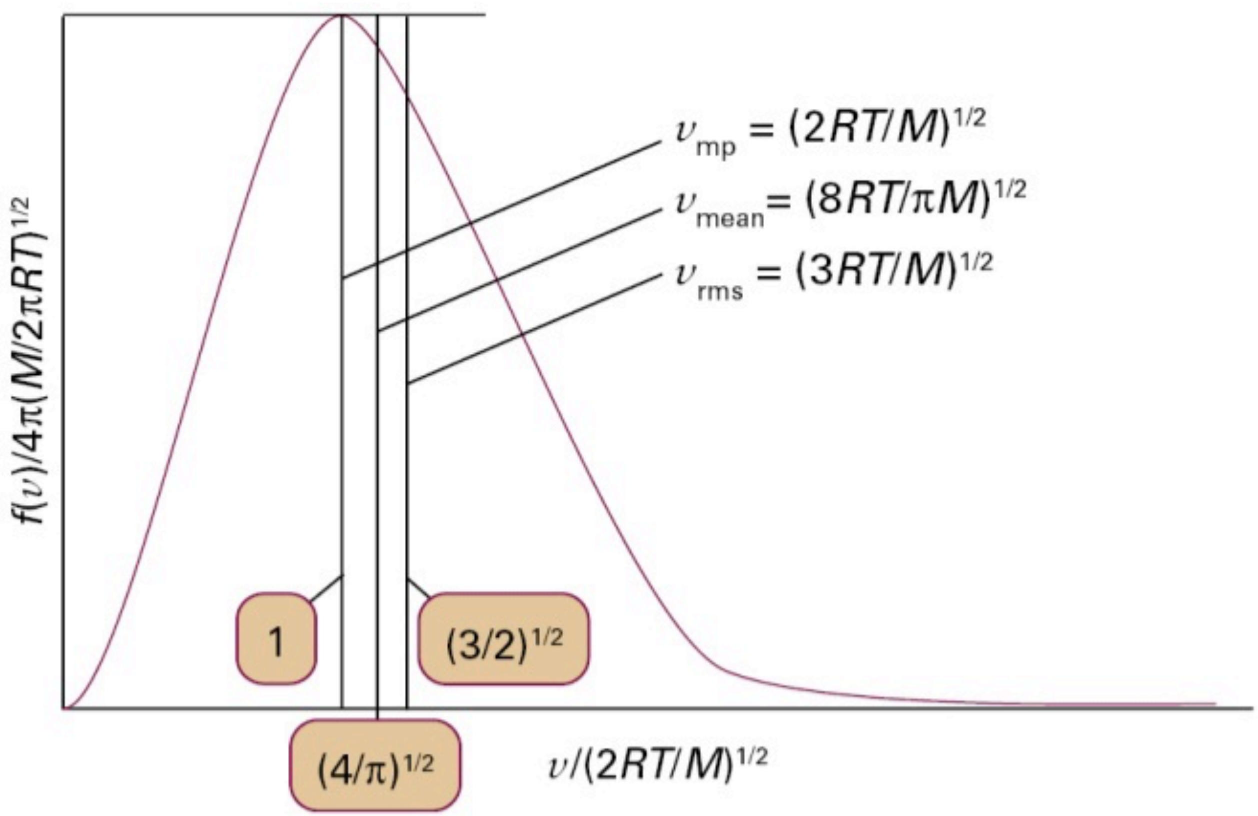
$$v_{rms} = \left(\int_0^\infty v^2 f\left(v\right) dv\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2}$$

Root mean square speed

For N_2(gas) at 25 °C

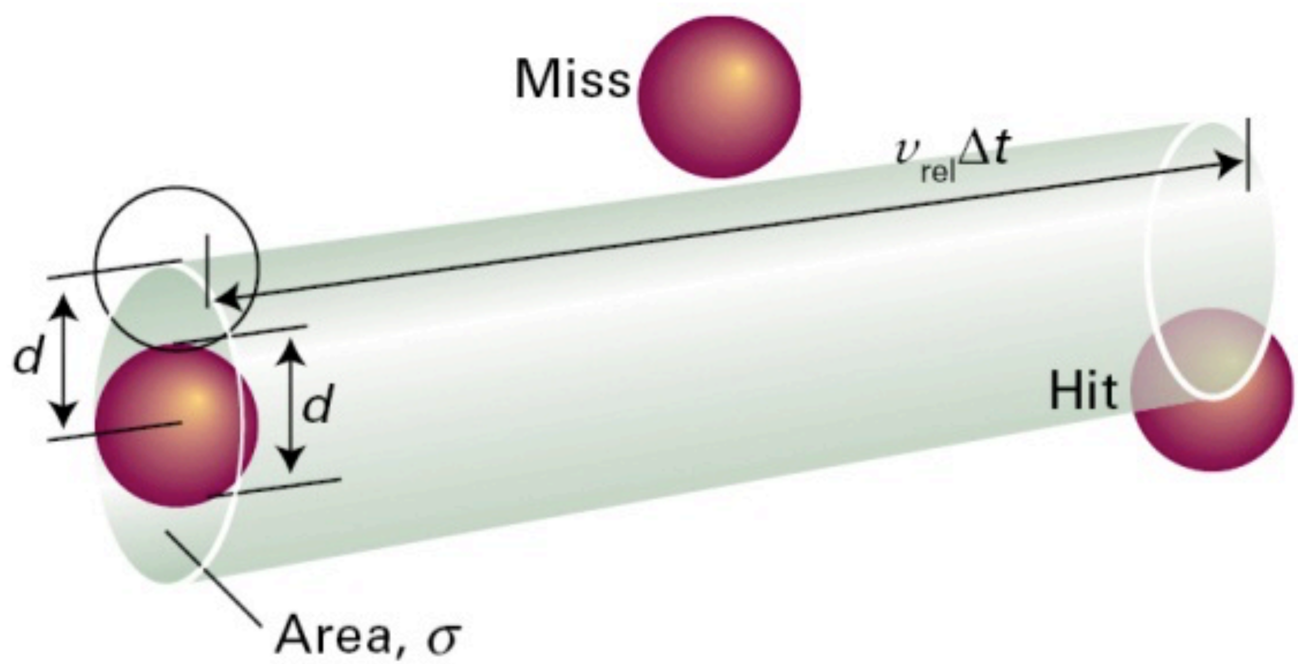
v_{mean} = 475 m/sec
V_{rms} = 515 m/sec

Summary of Speed Averages



Collisions

Define collision Cross Section: $\sigma = \pi d^2$



Collision frequency $z = \sigma v_{rel} N/V$

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

Mean Free Path

Average distance traveled between colllisions

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

Example: N_2(gas) at 25 °C and 1Atm pressure

$\lambda = 9.5 \times 10^{-8}$m

Diffusion and Transport

Molecules move randomly in straight paths between collisions.

FLUX

Flux (J) is the quantity of a property passing through a given area in a given time interval divided by the area and the time duration.

Flux of matter---"diffusion"
e.g. molecules/m^2sec

Flux doesn't have to be matter---e.g. could be energy, etc.

Fick's Law

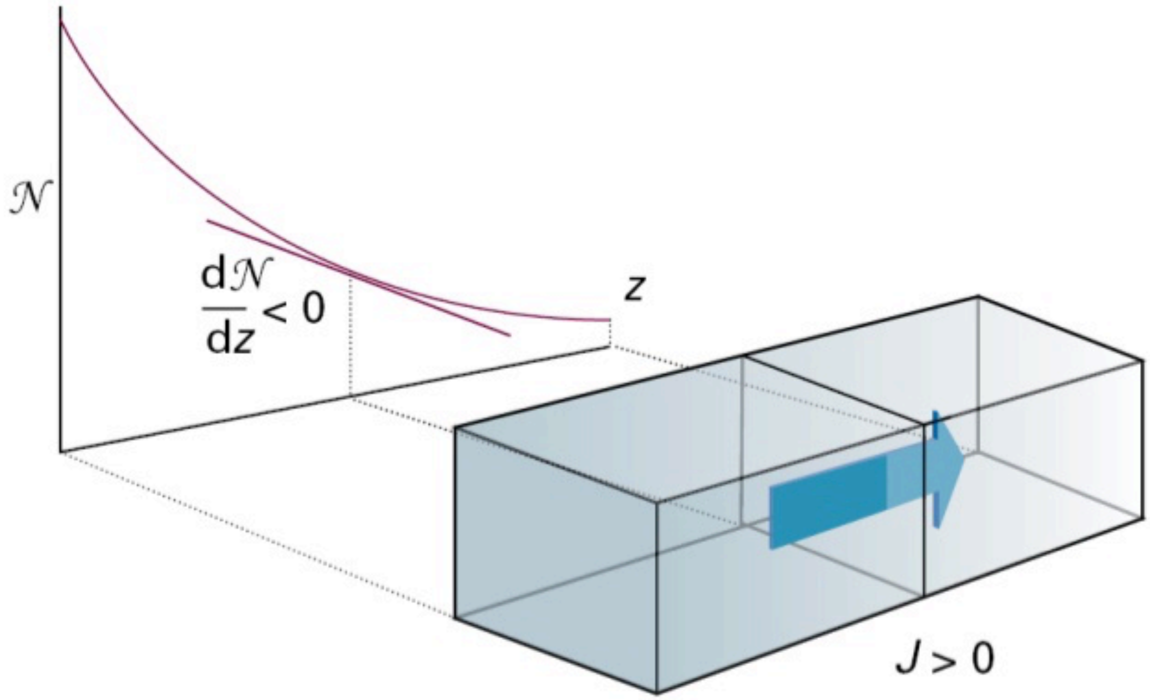
Empirically the flux is often related to the spatial first derivative of some related property.

$$J(matter) \approx \frac{dN}{dz}$$

Fick's first law

Concentration Gradient Leads to Diffusion

NET FLUX



Direction of Flux??

$$J(matter) = -D\frac{dN}{dz}$$

D = Diffusion Coeficient

UNITS?

$$J(matter) = -D\frac{dN}{dz}$$

$$\frac{dN}{dz}$$

Has units number•$m^{-3}m^{-1}$= number •m^{-4}

J should have units number•$m^{-2}sec^{-1}$

This means the units of D are: m^2sec^{-1}

Similar Equations for Other Properties

Thermal Energy Flux

$$J(thermalenergy) = -\kappa \frac{dT}{dz}$$

κ **Is the coeficient of thermal conductivity**

κ **Units are: $JK^{-1}m^{-1}s^{-1}$**
Js^{-1} = 1 Watt

κ **Units are often: $WK^{-1}m^{-1}$**

Since units of dT/dz are Km^{-1} the units of Thermal energy flux are: $Wm^{-2}s^{-1}$

Variation of thermal conductivity for different gases

Table 19A.1* Transport properties of gases at 1 atm

	$\kappa/(\mathrm{mW\ K^{-1}\ m^{-1}})$	$\eta/\mu\mathrm{P}$‡	
	273 K	273 K	293 K
Ar	16.3	210	223
CO_2	14.5	136	147
He	144.2	187	196
N_2	24.0	166	176

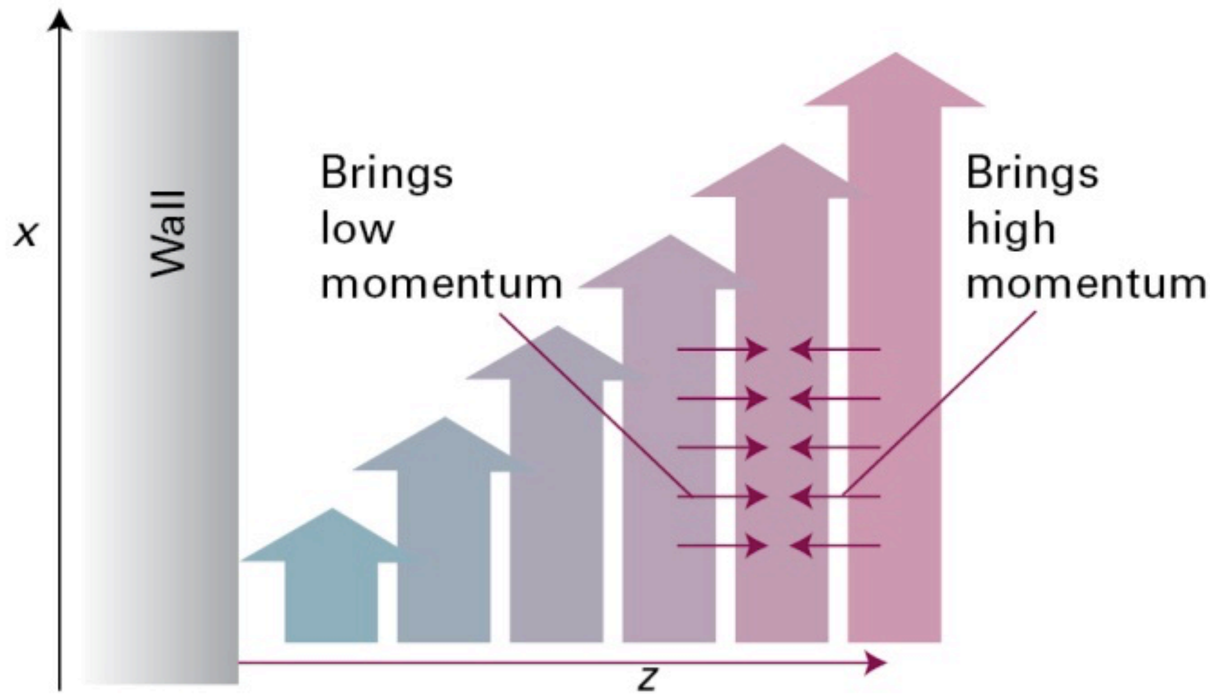
* More values are given in the *Resource section*.

‡ $1\,\mu\mathrm{P} = 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}$.

$$\boldsymbol{\kappa} \approx \mathbf{v}_{\mathbf{mean}}$$

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

FLUX OF MOMENTUM AND VISCOSITY



$$J(xmomentum) = -\eta \frac{dv_x}{dz}$$

η = coeficient of viscosity

THE END

SEE YOU FRIDAY