Physical Chemistry (Chem 132A)

Lecture 17
Wednesday, November 8

Homework #6 is due November 11

Schedule

1. This Friday (November 10) is a campus holiday so no lecture.

2. No Lecture next Monday, November 13

3. There will be a new WebAssign homework set (Homework #7) available on Saturday night (November 11). This will be due on November 18. This will probably be the last homework assignment before the second midterm.

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

Phase Rule

One component system:

$F = 3 - P$

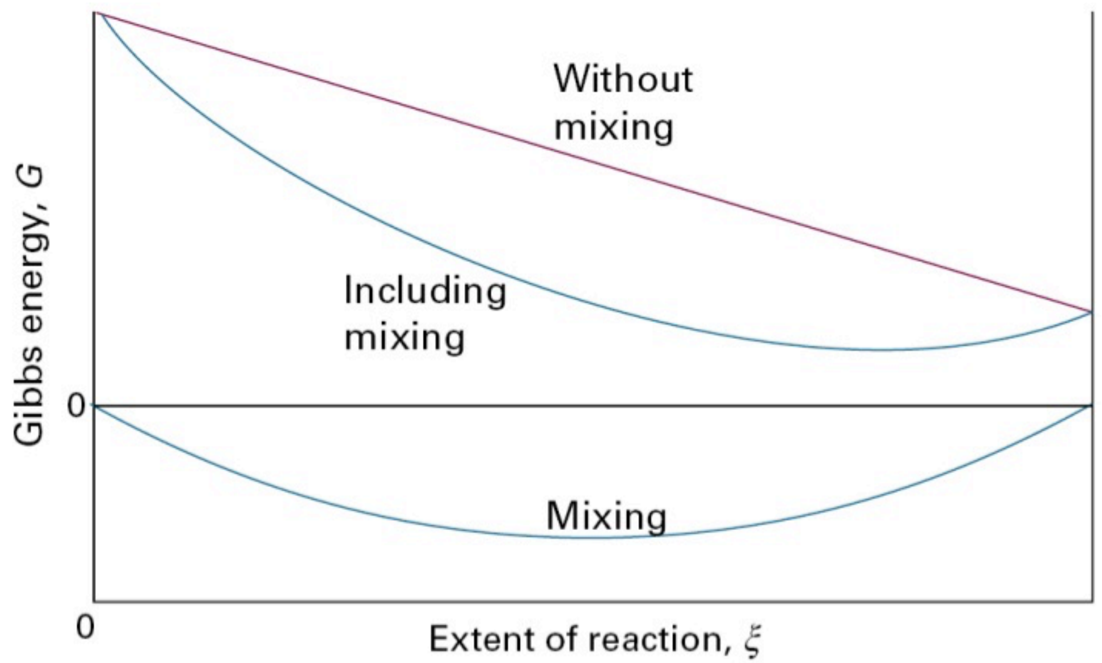
- **if $P = 1$, then $F = 2$**
- **if $P = 2$, then $F = 1$ (phase boundary line)**
- **if $P = 3$, then $F = 0$ (triple point)**

In General:

$F = C - P + 2$

- **For a 2 component system: $C = 2$**
- **$F = 4 - P$**

For A↔B (ideal gases) Mixing is important



Non-ideal case ΔH can contribute

Anything Different from Introductory Chemistry?

$$A + B \longleftrightarrow C + D$$

$$K = \frac{a_C a_D}{a_A a_B}$$

K should be written in terms of activities

$$K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C b_C \gamma_D b_D}{\gamma_A b_A \gamma_B b_b} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \frac{b_C b_D}{b_A b_B}$$

$$K = K_\gamma K_b$$

Temperature Dependence of K

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta_r H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Le Chatelier's Principle

Equilibrium shifts to offset any perturbation

Electrochemical Cells and Cell Potentials

Chapter 6C and 6D

You should know this material from Introductory Chemistry

Read and review 6C and 6D

- **Balancing half-reactions and overall Redox reactions**
- **Standard potentials**
- **Nernst Equation**

New Topic

Rates of Chemical Reactions
(Kinetics)

Text: Chapters 19, 20, 21

Spontaneous Reactions: Thermodynamics

May not happen rapidly: Kinetics

Classic Example:

C(graphite) $\Delta_f G^0 = 0$

C(diamond) $\Delta_f G^0 = +2.900$ kJ/mol

How do Reactions Occur?

$A + B \rightarrow C$

Collisions!!

How often do collisions occur?

Need to be "effective"
sufficiently energetic
correct orientation

Essential Background

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

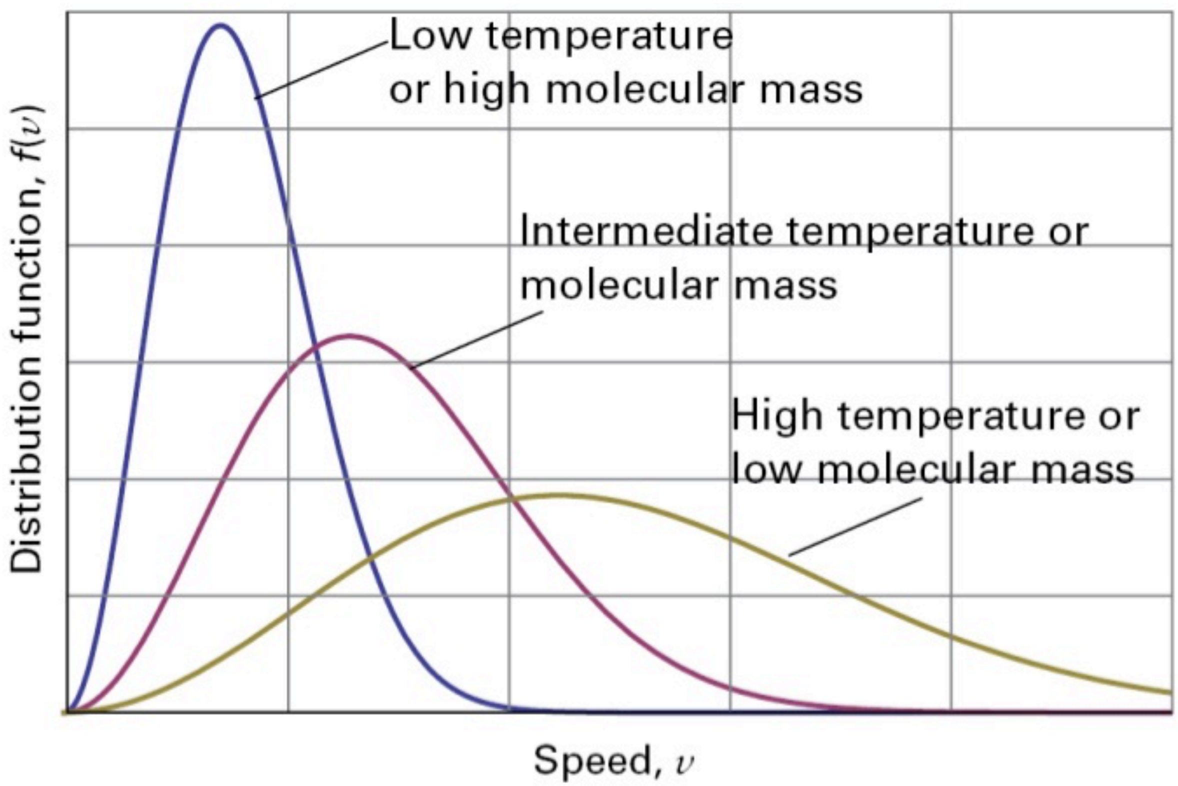
$$f\left(v\right) = Ke^{-\left(\frac{1}{2}mv_x^2+\frac{1}{2}mv_y^2+\frac{1}{2}mv_z^2\right)} = Ke^{-\left(\frac{1}{2}mv_x^2\right)}e^{-\left(\frac{1}{2}mv_y^2\right)}e^{-\left(\frac{1}{2}mv_z^2\right)} = f\left(v_x\right)f\left(v_y\right)f\left(v_z\right)$$

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

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

This can also be written in terms of M and R

Properties of the Boltzmann Speed Distribution



Calculation of Averages

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

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

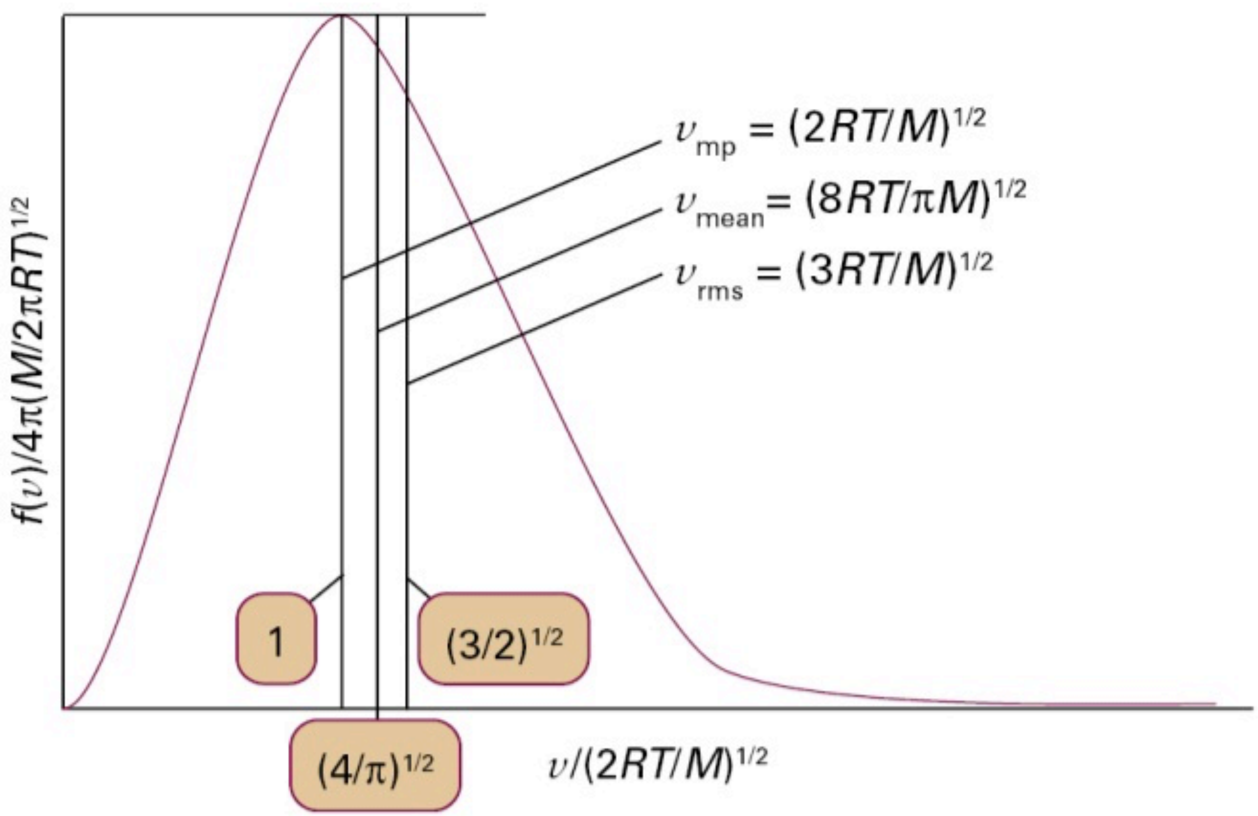
$$v_{rms} = \left(\int_0^\infty v^2 f(v)\,dv\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2}$$

Root mean square speed

For N_2(gas) at 25 °C

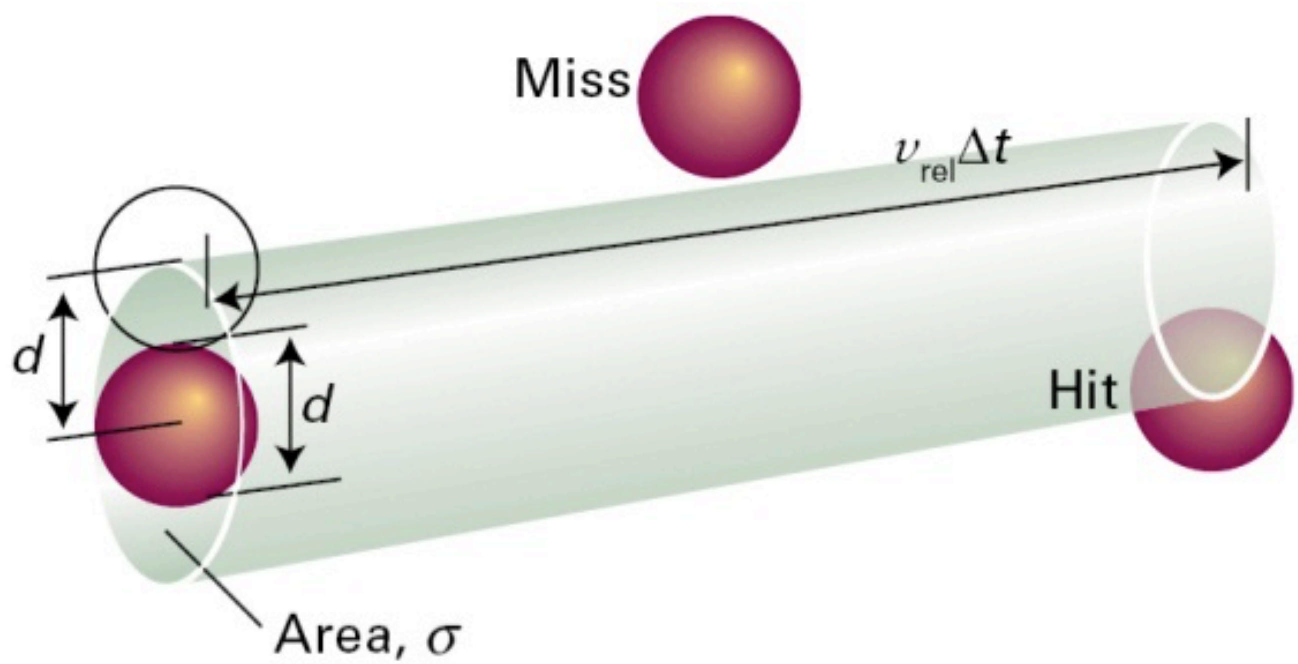
v_{mean} = 475 m/sec
V_{rms} = 515 m/sec

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

λ = 9.5 x 10^{-8}m

Diffusion and Tranport

Molecules move randomly in straight paths between collisions.

THE END

No lecture Friday (10th) or Monday (13th)

SEE YOU Wednesday (Nov. 15)