

Motions of Biological Molecules and Rates of Chemical Reactions Chapters 8 and 9

I was going home to dinner, past a shallow pool, which was green with springing grass, . . . when it occurred to me that I heard the dream of the toad. It rang through and filled all the air, though I had not heard it once. And I turned my companion's attention to it, but he did not appear to perceive it as a new sound in the air. Loud and prevailing as it is, most men do not notice it at all. It is to them, perchance, a sort of simmering or seething of all nature. That afternoon the dream of the toads rang through the elms by Little River and affected the thoughts of men, though they were not conscious that they heard it. How watchful we must be to keep the crystal well that we are made, clear!

THOREAU

Printed in book, The Second Law by Henry Bent

THOREAU

Henry Bent

In [human thermodynamics education](#), Henry Albert Bent (c.1927-) was is an American [physical chemist](#) noted for his 1965 book *The Second Law*, for his 1971 article “**Haste Makes Waste: Pollution and Entropy**”, in which he attempts at a connection between the maintenance of the environment and [entropy](#), and for his thermodynamics workshops, where he attempted to educate students on how to live ethically according to the [laws](#) of thermodynamics. [1]

Specifically, instead of a national energy policy, Bent states:

"What we need is a personal [entropy ethic](#)."

http://www.musicofnature.org/home/american_toad_dream/

Chapters 2-4,6,7: Thermodynamics

(equilibrium states)

All about what is possible or not
(never whether or how how fast)

Chapters 8-10: Study rate at which physical and chemical processes that are NOT AT EQUILIBRIUM
→ proceed to equilibrium

Chapter 9: Kinetics: rates of chemical reactions

Chapter 8: About processes that depend on how fast molecules move:

Diffusion

Sedimentation

Electrophoresis

first we examine velocities of molecules

From Lecture 4 this semester:

$$p = 2U_z/V \quad \text{therefore } pV = 2U_z = 2U_m/3 = nRT$$

$$U_m = (3/2) RT = \frac{1}{2} M \langle v^2 \rangle \quad (\text{where } M = \text{molecular wt.})$$

= Average Molar Translational Kinetic Energy

Now calculate the square root of the average of the square of the speed.

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

What is another word for average?

$$\text{The root mean square speed} = v_{rms} = (3RT/M)^{1/2}$$

The root mean square speed = $v_{rms} = (3RT/M)^{1/2}$

v_{rms} is the only speed you need for estimating

Example: N₂ (gas) at 300 K

$$\langle v^2 \rangle = \frac{3RT}{M}$$

$$\langle v^2 \rangle^{1/2} = \left(\frac{3RT}{M} \right)^{1/2} = \left(\frac{3 \times 8.3145 \times 300}{0.028} \right)^{1/2}$$

$$v_{rms} = 517 \text{ m/s} = 1700 \text{ ft/s}$$

This very close to the speed of sound!

Sound travels only by the motion of molecules

Boltzmann Distribution

We have seen how the Boltzmann equation allowed us to calculate the ratio of the **ratio of numbers** of molecules at **equilibrium** at different elevations in the atmosphere using the potential energy, mgh

Recall Gibbs, Boltzmann said, independently in ~1880

$$\frac{P_2}{P_1} = \frac{g_2}{g_1} e^{\frac{-(\Delta U)}{k_B T}} = e^{\frac{-(\Delta mgh)}{k_B T}} = e^{\frac{-(\Delta Mgh)}{RT}} \quad \text{Units } ????$$

where, g_2/g_1 is the ratio of number of microstates available in the two states.
i.e., same as we have called W_2/W_1 , where $\mathbf{S} = \mathbf{k}_B \ln \mathbf{W}$ also given by Boltzmann.

$g = W =$ “**degeneracy**” of the state was nearly independent of elevation

Maxwell-Boltzmann Distribution

Reading is Ch. 5, pp152-156 (for your information only); lecture notes are adequate.

is about the probability to find a molecule in different **kinetic energy** levels, $\frac{1}{2} m v_1^2$, and $\frac{1}{2} m v_2^2$, where we let $v_1 = 0$

http://en.wikipedia.org/wiki/Kinetic_theory_of_gases

$$\frac{P(v)}{P(0)} \propto v^2 e^{-\frac{1}{2}(mv^2)/k_B T} \propto v^2 e^{-\frac{1}{2}(Mv^2)/RT}$$

here the “degeneracy” of the state is proportional to the square of the speed, v^2 . More often written as a histogram, or frequency distribution:

$$N(v) \propto v^2 e^{-\frac{1}{2}(Mv^2)/RT}$$

where $N(v)$ is understood to be the number of molecules with speed lying between v and $v + dv$

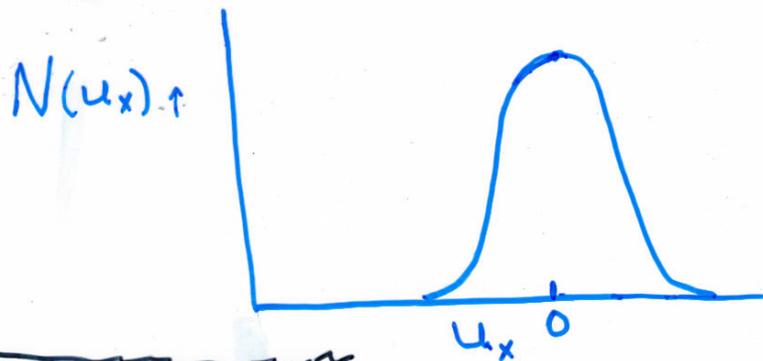
MAXWELL - BOLZMANN DISTRIBUTION (of velocities), u

$N(u_x)$ = number of molecules with velocity, u_x , between u_x and $u_x + du_x$

i.e., a frequency distribution

$$N(u_x) \propto e^{-\frac{E}{k_B T}} = e^{-\frac{1/2 m u_x^2}{kT}}$$

↑
proportional



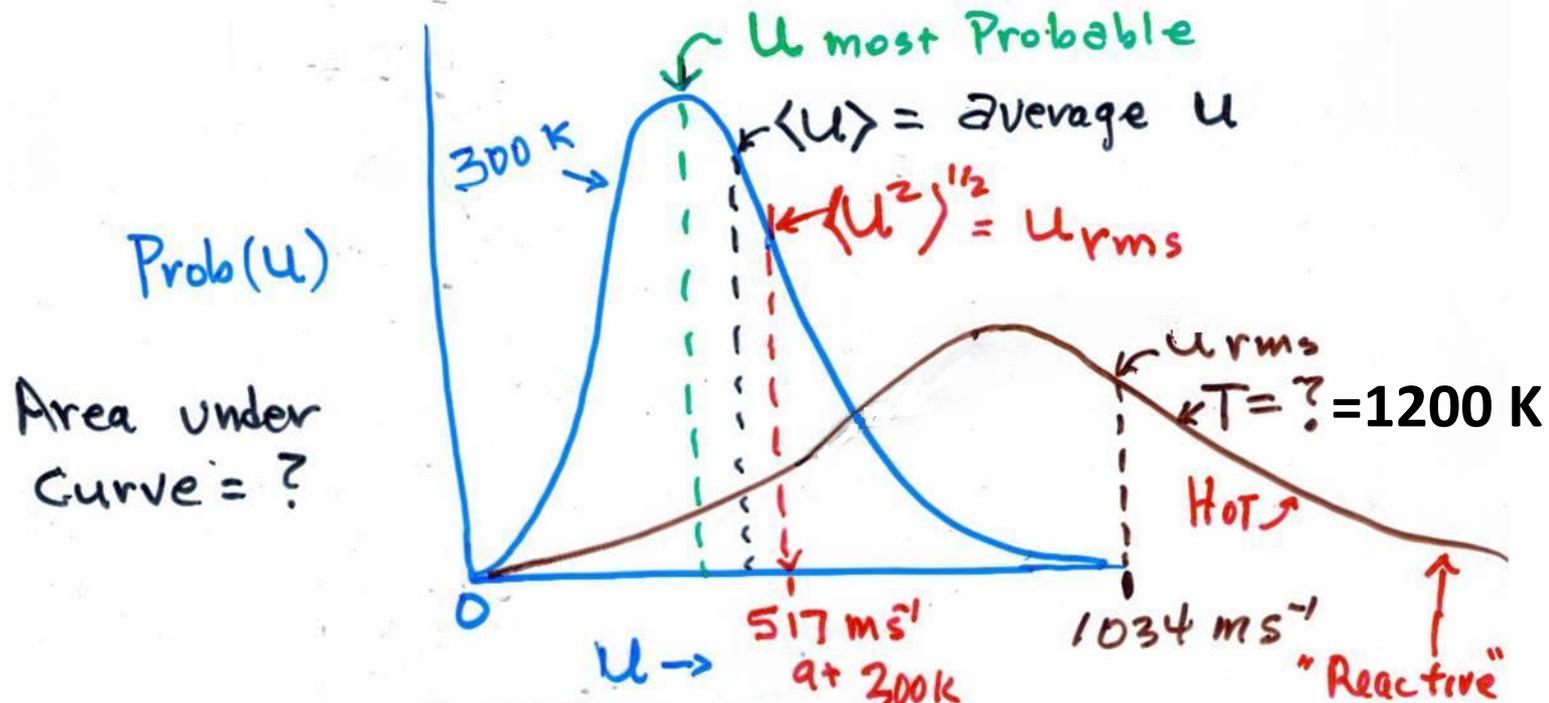
SPEED DISTRIBUTION

$$\text{Speed} = u = |\vec{u}|$$

$$N(u) \propto e^{-\frac{E}{kT}} = u^2 e^{-\frac{1/2 m u^2}{kT}}$$

↑
degeneracy

Prob(u) \propto Probability to observe u between $u \pm \Delta u$



$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

1.22

$$\langle u \rangle = \sqrt{\frac{8}{\pi} \frac{RT}{M}} = \sqrt{2.546 RT}$$

1.12

$$u_{most\ prob.} = \sqrt{2 \frac{RT}{M}}$$

1

Next we are going to get some ideas about some things you might be curious about that lead to:

estimates of rates of diffusion and rates of chemical reactions

1. how many collisions per second a molecule suffers = z (*little z*)
2. how many **total** collisions per second happen in a **cubic meter** of gas = Z (*big Z*)
3. how FAR a molecule travels between collisions = “**mean free path**”

The text has formulas for 3 kinds of “average speeds” used in the expressions for these 3 things, BUT THEY ARE ALL ESTIMATES.

Why? Because they are all the collisions of marbles flying around and colliding!

$$u_{rms} = \sqrt{\frac{3RT}{M}} \quad 1.22$$

$$\langle u \rangle = \sqrt{\frac{8}{\pi} \frac{RT}{M}} = \sqrt{2.546 RT} \quad 1.12$$

$$u_{most\ prob.} = \sqrt{2 \frac{RT}{M}} \quad 1$$

Because real molecules **are not marbles**, in this course, **THESE ARE ALL the SAME rough estimate**. We will always use v_{rms} because it so easy to calculate from $1/2Mv^2 = 3/2 RT$

COLLISIONS PER SECOND PER MOLECULE

$= Z \leftarrow$ (lower case z)

Proportional to: (SPEED) \times (HOW CROWDED) \times (HOW WIDE)

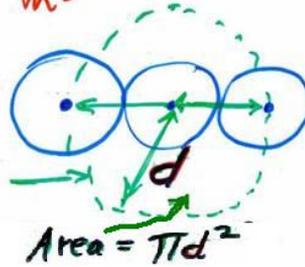
i.e. to: Average Velocity $\left(\frac{m}{s}\right) \times$ CONC $\left(\frac{\text{molecules}}{m^3}\right) \times$ AREA (m^2)

Units

$$Z = \sqrt{2} \langle u \rangle \times \frac{N}{V} \times \pi d^2$$

↑ relative speed factor. ↑ ave speed ↑ molecules / m³ ↑ Collision area.

$d =$ molecular diameter
 $=$ collision radius



For N₂ $\langle u \rangle \cong 500 \text{ m s}^{-1}$

At 1 atm & 300K $\frac{N}{V} = 6 \times 10^{23} \frac{n}{V} = 6 \times 10^{23} \frac{P}{RT} \leftarrow \text{(ideal gas law)}$

$$= 6 \times 10^{23} \times \frac{1 \text{ atm}}{0.0821 \text{ Latm} / \text{mol K} \times 300} \times \frac{10^3 \text{ L}}{m^3}$$

$$= 2.5 \times 10^{25} \text{ molecules/m}^3$$

$$G \cong 4A = 4 \times 10^{-10} \text{ m} \quad \pi d^2 \cong (3.14)(4 \times 10^{-10})^2 = 50 \times 10^{-20} \text{ m}^2$$

$$Z = \sqrt{2} \cdot 500 \frac{m}{s} \cdot 2.5 \times 10^{25} \frac{\text{molecules}}{m^3} \cdot 50 \times 10^{-20} \text{ m}^2$$

$$= 9 \times 10^9 \cong 10^{10} \frac{\text{collisions}}{\text{sec molecule}}$$

BIG Z = total collisions / $m^3 s$
(of all molecules)

$$\begin{aligned} Z &= Z \text{ (Coll. } s^{-1} \text{ molecule}^{-1}) \times \frac{N}{V} \frac{\text{molecules}}{m^3} \times \frac{1}{2} \\ &= 10^{10} \times 2.5 \times 10^{25} \times \frac{1}{2} \\ &\approx 10^{35} \text{ collisions } s^{-1} m^{-3} \end{aligned}$$

↑
Why?

Note $\frac{N}{V} = \frac{P}{k_B T}$

$$PV = nRT = Nk_B T$$

MEAN FREE PATH = ^{average} distance between collisions

$$= \frac{\text{meters}}{\text{Collision}} = \frac{\text{m s}^{-1}}{\text{Coll. s}^{-1}} = \frac{\langle U \rangle}{z}$$

$$\approx \frac{500 \text{ m s}^{-1}}{10^{10} \text{ coll. s}^{-1}} = 5 \times 10^{-8} = 50 \text{ nm}$$

(for N_2 @ 1 atm 300K)

what if $P = 10^{-10}$ atm?

We made the P 10^{10} times smaller

What happens to z, the collisions/sec per molecule?

Obviously, the mean free path gets 10^{10} times longer