10/29/01 Ave = 73 ± 17 Median = 77 (39-99)

<u>Note</u> $k = \frac{R}{N_0}$

$k \Rightarrow$ per molecule

$R \Rightarrow$ per mole

Whenever you see k, it's per <u>molecule</u>

Whenever you see R, it's per <u>mole</u>

<u>BIG PICTURE</u> $\rightarrow$ every molecule has an <u>average</u> kinetic energy of $\frac{3}{2}kT$

DISTRIBUTIONS about the <u>average</u>

<u>MAXWELL - BOLTZMANN</u>

BOLTZMANN $\Rightarrow$

Probability of finding a molecule in state i w/ energy E_i

$$P_i \propto e^{-E_i/kT}$$

If there are g_i states w/ energy E_i then

Probability of finding a molecule w/ energy E_i $\rightarrow$

$$P_i \propto \underbrace{g_i}_{\text{degeneracy}} e^{-E_i/kT}$$

N. B.

IMPORTANT EQUATION!

P_j is relative to all other P_j's

$\underbrace{e^{-\Delta H/RT}}_{\text{per mole}}$

$$P_j = \frac{g_j e^{-E_j/kT}}{\sum g_i e^{-E_i/kT}} = \frac{N_j}{N_{TOT}}$$

(Remember $\sum^{ALL} P_j = 1$)

SAVE we'll use often

$\Downarrow$ Also

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

SKIP SOME DERIVATIONS

mean speed (not velocity) $\langle u \rangle = \left(\frac{8kT}{\pi m} \right)^{1/2}$

mean square speed (or velocity) $\langle u^2 \rangle = \frac{3kT}{m}$

Molecular Collisions – First step to a reaction.

Root mean square speed $= \sqrt{\langle u^2 \rangle} = \sqrt{\frac{3kT}{m}} = 218 \, m \, s^{-1}$ rose scent at R.T.

Intuition says "wait a minute!"

Collisions slow the NET diffusion

Diff: Walk across an empty room
Walk across a crowded room, drunk(!) (random)

Collisions per sec = z for 1 molecule

Q: Proportional to what?

A: Conc $\left(\frac{N}{V}\right)$
Speed (u)
Size (σ)

cross section

Real answer:

$$z \propto \frac{N}{V}\sigma^2\langle u\rangle$$

Actually $z = \sqrt{2}\,\pi\,\frac{N}{V}\sigma^2\langle u\rangle \Rightarrow \left(\frac{\text{molec}}{\text{cm}^3}\right)\left(\text{cm}^2\right)\left(\frac{\text{cm}}{\text{sec}}\right)$

Plugging in for $\langle u\rangle$

$$z = 4\sqrt{\pi}\,\frac{N}{V}\sigma^2\left(\frac{RT}{M}\right)^{1/2}$$

Total # Collisions $\quad \frac{N}{V} \Rightarrow \frac{\text{molec}}{\text{Volume}}$

$\therefore \frac{N}{V}z \Leftarrow \frac{\text{molecules colliding}}{(\text{Volume})(\text{time})}$

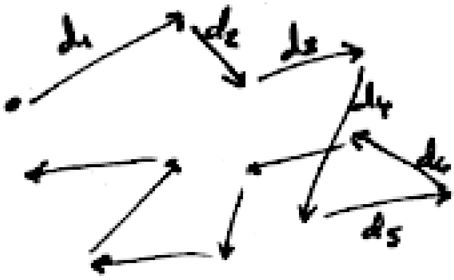
$$\frac{\text{Collisions}}{\text{vol}\cdot\text{time}} = Z = \left(\frac{N}{V}\right)\frac{z}{2} = 2\sqrt{\pi}\left(\frac{N}{V}\right)^2\sigma^2\left(\frac{RT}{M}\right)^{1/2}$$

~~"Self" collisions~~ Don't count each collision twice

Mean Free Path ⇒ average distance between collisions

Brownian Motion

Random Walk



$$l = \frac{\langle u \rangle}{Z} = \frac{\text{dist/time}}{\text{collisions/time}}$$

$$l = \frac{1}{\sqrt{2}\,\pi \left(\frac{N}{V}\right) \sigma^2}$$

$$\langle d^2 \rangle = \frac{\sum^{\#\text{paths}} d_i^2}{\#\text{ paths}}$$

$$= N l^2$$

$$\sqrt{\langle d^2 \rangle} = \sqrt{N}\, l \Leftarrow \text{Applications } \underline{\underline{\text{everywhere}}}.$$

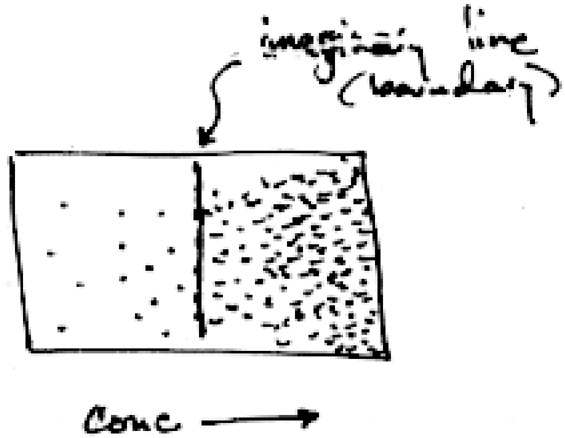
<u>GAS MOLECULES</u>

$$\cancel{(\langle d^2 \rangle)^{1/2} = \sqrt{Z}\, l = \frac{\langle u \rangle}{\sqrt{Z}}}$$

$$\langle d^2 \rangle = \frac{\langle u^* \rangle^2}{Z}$$

$$(\langle d^2 \rangle)^{1/2} = \frac{\langle u \rangle}{\sqrt{Z}}$$

Diffusion



Probability that
any molecule
crosses from left to
right is much lower
than that for any molecule
moving from right to left ← Purely intuitional
common sense

$J_x \equiv$ net amount of molecules crossing the boundary per unit time.

$$J_x \propto -\frac{dc}{dx}$$ ← magnitude of the gradient

$$J_x = -D\frac{dc}{dx}$$

But as diffusion occurs, the gradient lessens.
∴ J_x slows

$$\left(\frac{dc}{dt}\right)_x = D\left(\frac{d^2c}{dx^2}\right)_t$$

Change in Concentration w/ time $\propto$ 2ND derivative of change in conc w/ resp to x.

(D assumed to be indep of C)