11/5/99

Then f_x = (momentum change/collision)(# collisions/sec)

$$= (2mu_x)\left(\frac{u_x}{2l}\right)$$

$$\Rightarrow \quad = \frac{mu_x^2}{l}$$

Pressure $\Rightarrow P = f_x/A = \frac{f_x}{l^2} = \frac{mu_x^2}{l^3}$ (per molecule)

For N identical, ideal molecules

$$F_x = \frac{mu_{x_1}^2}{l} + \frac{mu_{x_2}^2}{l} + \frac{mu_{x_3}^2}{l} + \cdots + \frac{mu_{x_N}^2}{l}$$

$$= \sum \frac{mu_{x_i}^2}{l}$$

$$= \frac{m}{l} \sum^{N} u_{x_i}^2$$

Pressure $P = \frac{F_x}{l^2} = \frac{m}{l^3} \sum^{N} u_{x_i}^2$

$$= \frac{m}{V} \sum u_x^2$$ V = volume = l^3

Define: "mean-square velocity (speed)"

$$\Rightarrow \langle u_x^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} u_{x_i}^2$$

"averaged"

along x dimension

$$P = \frac{Nm}{V} \langle u_x^2 \rangle$$

$$u_i^2 = u_{x_i}^2 + u_{y_i}^2 + u_{z_i}^2$$

$$\therefore \quad \frac{1}{N}\sum u_i^2 = \frac{1}{N}\sum u_{x_i}^2 + \frac{1}{N}\sum u_{y_i}^2 + \frac{1}{N}\sum u_{z_i}^2$$

Define $\langle u^2 \rangle = \frac{1}{N}\sum u_i^2$

$$\therefore \quad \langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle$$

For random movement, should all be the same.

$$\therefore \quad \langle u^2 \rangle = 3\langle u_x^2 \rangle$$

$$\therefore \quad P = \frac{Nm}{V}\langle u_x^2 \rangle = \frac{1}{3}\frac{Nm}{V}\langle u^2 \rangle$$

From IDEAL GAS LAW:

$$P = \frac{\frac{N}{N_0}RT}{V} = \frac{1}{3}\frac{Nm}{V}\langle u^2 \rangle \qquad n = \frac{N}{N_0}$$

$$\Rightarrow \frac{RT}{N_0} = \frac{1}{3} m \langle u^2 \rangle$$

$$\overline{U}_{TR} \Rightarrow \frac{1}{2} N_0 m \langle u^2 \rangle$$ translational kinetic energy per mole

means "per mole"

$$RT = \frac{2}{3}\overline{U}_{tr} \quad \text{or} \quad \overline{U}_{tr} = \frac{3}{2}RT$$

Relates (directly) translational kinetic energy and tempe

Kinetic energy depends ONLY on T!

Same equation we saw back on p. ___

$N_0 m = M$ = molar mass

So,

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

$$\sqrt{\langle u^2 \rangle} = \sqrt{\frac{3RT}{M}}$$ Root mean square velocity (speed)

Calculate for O_2 → at 20°C $\langle u^2 \rangle^{1/2} = 478\ m\ s^{-1}$

(FAST!)

But smells don't migrate across the room that fast!

Why?

Bottom Line → $\sqrt{\langle u^2 \rangle}$ is directly related to temperature

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Probability Distributions — Go on about statistics of large numbers!

The probability of finding a (gas) molecule with energy E_i → $P_i \propto g_i e^{-E_i/kT}$

Maxwell-Boltzmann ⟶

degeneracy – number of different states of ~~the~~ a molecule with energy E_i

So to Compare the probabilities of finding molecules with two different energies (in other words: the ratio of the # of molecules with the two energies):

$$\frac{P_j}{P_i} = \frac{N_j}{N_i} = \frac{g_j e^{-E_j/kT}}{g_i e^{-E_i/kT}} = \frac{g_j}{g_i} e^{-(E_j - E_i)/kT}$$

At equilibrium

Individual Probabilities are then →

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

⇐ Boltzmann- "Most Probable" (Equilibrium) Distribution

⇐ A VERY IMPORTANT EQUATION!

Now apply to kinetic energy of gases $E = \frac{1}{2}mu^2$

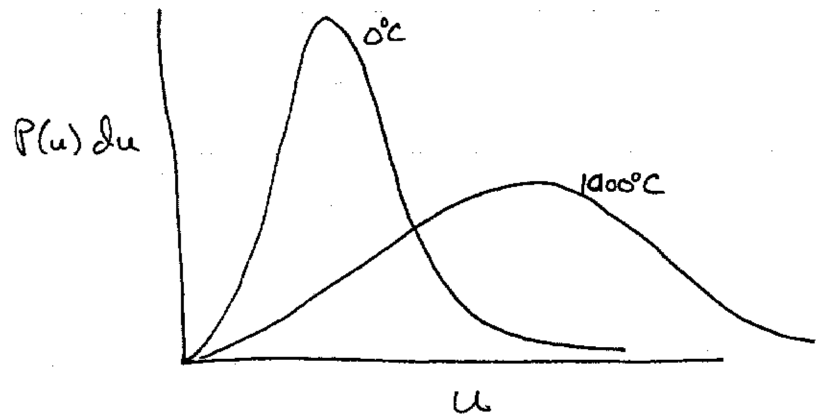
$$P(u_j) = \frac{e^{-\frac{mu_j^2}{2kT}}}{\sum_i e^{-\frac{mu_i^2}{2kT}}}$$

Integral/Differential

The probability of finding between u and du ⇒ $P(u)\,du = \dfrac{u^2 e^{-mu^2/2kT}\,du}{\int_0^\infty u^2 e^{-mu^2/2kT}\,du}$

Jump to result:

$$P(u)\,du = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} u^2 e^{-mu^2/2kT}\,du$$



At higher temperatures it's more likely to find molecules with higher velocities

The distribution also gets wider with higher temperature.

Calculate averages $\quad \langle u \rangle = \int_0^\infty u\, P(u)\,du = \left(\frac{8kT}{\pi m}\right)^{1/2}$

$$\langle u^2 \rangle = \int_0^\infty u^2 P(u)\,du = \frac{3kT}{m}$$

$$\sqrt{\langle u^2 \rangle} = \left(\frac{3kT}{m}\right)^{1/2}$$

Remember that on a molar basis R replaces k
and M replaces m

$\langle u \rangle = \left(\frac{8RT}{\pi M}\right)^{1/2} \qquad \langle u^2 \rangle = \frac{3RT}{M}$

LIQUIDS AND SOLIDS SIMILAR, BUT MORE COMPLEX (non-ideal)