

CHEM 26300 (Chemical Kinetics and Dynamics) Notes

Steven Labalme

March 28, 2022

Contents

27 Kinetic Theory of Gases	1
27.1 Background and Ideal Gas Distributions	1
References	4

List of Figures

27.1 Important values of molecular speed.	2
---	---

Chapter 27

Kinetic Theory of Gases

27.1 Background and Ideal Gas Distributions

3/28:

- Learning objectives for CHEM 263.
 - The time-dependent phenomena.
 - Reaction rate and rate laws.
 - Reaction mechanisms and reaction dynamics.
 - Surface chemistry and catalysis.
 - Experimental design and instruments.

- Before we move into the content of CHEM 263, a few important notes from CHEM 262.

- **Partition function** (for a system with N states): The following function of temperature. *Denoted by $Q(T)$. Given by*

$$Q(T) = \sum_{n=1}^N e^{-E_n/k_B T}$$

- **Observable:** A quantum mechanical operator.
- Consider a system described by the partition function Q . Let $|i\rangle$ denote the state with energy E_i , and let A be an observable. Then the expected value of the observable A is given by

$$\langle A \rangle = \frac{1}{Q} \sum_{|i\rangle} \langle i|A|i\rangle e^{-E_i/k_B T}$$

- “This fundamental law is the summit of statistical mechanics, and the entire subject is either the slide-down from this summit, as the principle is applied to various cases, or the climb-up to where the fundamental law is derived and the concepts of thermal equilibrium and temperature T clarified” Richard Feynman, Statistical Mechanics.
- Now onto the CHEM 263 content.
- Tian duplicates the derivation of the ideal gas law given on Labalme (2021, pp. 18–19).
 - Note that if M is the molar mass, m is the mass of a single molecule, N_A is Avogadro’s number, N is the number of particles present, and n is the number of moles present, then since $N/N_A = n$ and $M/N_A = m$, we have that

$$M = \frac{Nm}{n}$$

- Important values of molecular speed u .

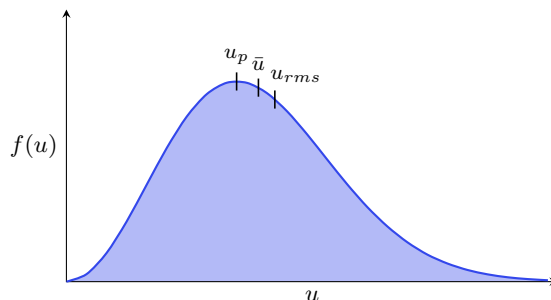


Figure 27.1: Important values of molecular speed.

- **Maxwell Speed Distribution Function:** The following normalized function, which gives the probability that a particle in an ideal gas will have a given speed. Denoted by $f(u)$. Given by

$$f(u) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} u^2 \exp \left(-\frac{Mu^2}{2RT} \right)$$

- **Most probable speed:** The speed that a particle in an ideal gas is most likely to have. Denoted by u_p . Given by

$$u_p = \sqrt{\frac{2RT}{M}}$$

- **Mean speed:** The average speed of all of the particles in an ideal gas. Denoted by \bar{u} . Given by

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}}$$

- **Root mean squared speed:** The square root of the average of the speeds squared. Denoted by u_{rms} . Given by

$$u_{rms} = \langle u^2 \rangle^{1/2} = \sqrt{\frac{3RT}{M}}$$

- The distributions of the molecular speed and velocity components are different.
 - While speed follows the Maxwell-Boltzmann distribution, velocity follows (on each Cartesian axis) a Gaussian distribution centered at zero.
 - At higher temperatures, both distributions “flatten out,” but maintain their shape.
- Deriving the distribution of the velocity component.
 - The velocity components are independent.
 - Let

$$h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

be the distribution of speed with velocity components between $u_x, u_x + du_x$, $u_y, u_y + du_y$, and $u_z, u_z + du_z$, where $f(u_i)$ is the probability distribution of components i .

- Note that $h(u)$ is *not* the speed distribution with velocity components between $u, u + du$.
- Clever step: Note that the logarithmic form of the above equation leads to

$$\begin{aligned} \ln h(u) &= \ln f(u_x) + \ln f(u_y) + \ln f(u_z) \\ \left(\frac{\partial \ln h}{\partial u_x} \right)_{u_y, u_z} &= \frac{d \ln h}{du} \left(\frac{\partial u}{\partial u_x} \right)_{u_y, u_z} \\ &= \frac{u_x}{u} \frac{d \ln h}{du} \end{aligned}$$

where we evaluate $\partial u / \partial u_x$ by using the generalized Pythagorean theorem definition of u .

- Additionally, we have that

$$\left(\frac{\partial \ln h}{\partial u_x} \right)_{u_y, u_z} = \frac{d \ln f(u_x)}{du_x}$$

since the $\ln f(u_i)$ ($i \neq x$) terms are constant with respect to changes in u_x .

- Thus, combining the last two results, we have that

$$\frac{d \ln h(u)}{u du} = \frac{d \ln f(u_x)}{u_x du_x}$$

- It follows since the gas is isotropic that

$$\frac{d \ln h(u)}{u du} = \frac{d \ln f(u_x)}{u_x du_x} = \frac{d \ln f(u_y)}{u_y du_y} = \frac{d \ln f(u_z)}{u_z du_z}$$

- But since the three speed components are independent of each other, the above term is constant.
- It follows if we call the constant -2γ that

$$\begin{aligned} \frac{d \ln f(u_i)}{u_i du_i} &= -2\gamma \\ f(u_i) &= A e^{-\gamma u_i^2} \end{aligned}$$

for $i = x, y, z$.

- We will pick up with solving for A and γ in the next lecture.

References

Labalme, S. (2021). *PHYS 13300 (Waves, Optics, and Heat) notes*. Retrieved January 11, 2022, from <https://github.com/shadypuck/PHYS13300Notes/blob/master/Notes/notes.pdf>