An Alternative Derivation of Gas Pressure Using the Kinetic Theory

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Abstract: The kinetic theory is used to derive the pressure of an ideal gas assuming that the gas occupies a spherical container of diameter *D*.

General chemistry and physical chemistry texts that use the kinetic theory to derive the pressure of an ideal gas do so by studying a gas in a cubic or rectangular container [1]. The purpose of this note is to outline this derivation for a gas in a spherical container. A visual representation of this approach in coordinate and momentum space is provided in Figure 1.

A sphere of diameter D contains gas molecules moving randomly, executing elastic collisions with each other and the surface of the container as postulated by the kinetic theory.

Consider a molecule labeled i of mass m and velocity v_i making a collision with the surface at an angle θ relative to the perpendicular to the surface. The momentum transferred to the container in the direction perpendicular to the surface by the collision is

$$\Delta\left(mv\right)_{\text{surf}} = 2mv_i\cos\left(\theta\right) \tag{1}$$

Because the molecule travels a distance $D\cos(\theta)$ between collisions with the surface, the time interval (Δt) between collisions is

$$\Delta t = \frac{D\cos\left(\theta\right)}{v_i} \tag{2}$$

The force (F) exerted on the surface is the rate of momentum transfer,

$$F_i = \frac{\Delta\left(mv\right)_{\text{surf}}}{\Delta t} = \frac{2mv_i^2}{D} \tag{3}$$

Pressure (P) is force divided by area (A) and the surface area of a sphere is πD^2. The volume of a sphere (V) is $1/6\,\pi D^3$, therefore

$$P_i = \frac{F_i}{A} = \frac{2mv_i^2}{\pi D^3} = \frac{mv_i^2}{3V} \tag{4}$$

For a mole of gas molecules the total pressure is

$$P = \sum_i^{N_A} P_i = \frac{m}{3V}\sum_i^{N_A} v_i^2 = \frac{M\left\langle v^2\right\rangle}{3V} = \frac{2\left\langle KE\right\rangle}{3V} \tag{5}$$

where

$$\left\langle v^2\right\rangle = \frac{1}{N_A}\sum_i^{N_A} v_i^2$$

and $M = N_A m$.

As Dewey Carpenter pointed out many years ago [2], it is through a comparison of eq 5 with the ideal gas law that we conclude that the average molar kinetic energy of a gas is proportional to its absolute temperature

$$\left\langle KE\right\rangle = \frac{1}{2}M\left\langle v^2\right\rangle = \frac{3}{2}RT \tag{6}$$

Unfortunately most introductory texts incorrectly include this result as a postulate of the kinetic theory [3]. With regard to the formal assumptions of the kinetic theory Carpenter noted [2], "No reference is made in these postulates to the property of temperature. This is because the kinetic theory is a purely mechanical theory, whereas the concept of temperature belongs to the discipline of thermodynamics."

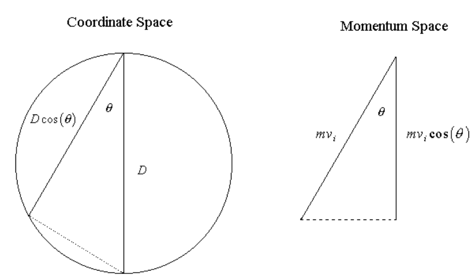

Figure 1. Coordinate and momentum space representations of a gas molecule in a spherical container colliding with the surface at an angle θ relative to the perpendicular to the surface.

References and Notes

1. See for example, Zumdahl, S. S.; Zumdahl, S. A. *Chemistry*, 5th ed.; Houghton Mifflin Co.: Boston, 2000; pp A14–A16; Atkins, P. W. *Physical Chemistry*, 6th ed.; W. H. Freeman and Co.: New York, 1998; pp 23–25.
2. Carpenter, D. K. *J. Chem. Educ.* **1966,** *43,* 332.
3. A survey of 15 currently available general chemistry textbooks revealed that ten included eq 6, or some form of it, as an assumption of the kinetic theory.