

IDEAL GAS: RELATION OF AVERAGE SPEED OF MOLECULES TO TEMPERATURE

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 1.18 - 1.20.

By using the ideal gas law and an analysis on the molecular scale, we can derive a relation between the speed of the molecules in an ideal gas and the temperature. Schroeder does this in detail in his section 1.2 so I won't go through the whole derivation again; I'll just summarize the main ideas.

The model places a single molecule inside a cylinder with a movable piston at one end. The molecule is moving at some speed v and whenever it hits a wall or the piston it bounces off elastically. If the axis of the cylinder is the x axis, then whenever the molecule hits the piston, the x component of its velocity, v_x , is reversed, which means that its x momentum changes by $\Delta p_x = -2mv_x$. The rate of change of momentum is the force exerted on the piston, and the force per unit area is the pressure, so we can relate v_x to the pressure exerted on the piston. Since we're considering only one molecule, the pressure is felt only at the moments when the molecule collides with the piston, so what we're really interested in is the time average of the pressure. It turns out that this is

$$\bar{P} = \frac{mv_x^2}{V} \quad (1)$$

where m is the mass of the molecule and V is the volume of the cylinder.

We can now extend the argument by putting a large number N of molecules in the cylinder. In this case, the v_x^2 factor is replaced by the average of v_x^2 over all the molecules, so we get

$$\bar{P}V = Nm\overline{v_x^2} \quad (2)$$

Comparing with the ideal gas law

$$PV = NkT \quad (3)$$

we see that

$$m\overline{v_x^2} = kT \quad (4)$$

or, since $\frac{1}{2}m\overline{v_x^2}$ is the kinetic energy from the x motion of the molecules,

$$\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}kT \quad (5)$$

However, since the molecules are moving at random, there's nothing special about the x direction, so we'd expect the same contribution to the kinetic energy from the y and z directions, giving the relation

$$\bar{K}_{trans} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT \quad (6)$$

where \bar{K}_{trans} is the average kinetic energy due to the translational motion of the molecules (if the molecules contain two or more atoms, then we can also have rotational and vibrational kinetic energy, so the total kinetic energy is greater than $\frac{3}{2}kT$).

A reasonable estimate of the average speed of molecules is the *root mean square* speed, defined as

$$v_{rms} \equiv \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} \quad (7)$$

Example 1. The molecules in a gas at room temperature are actually moving pretty fast. For example, for a nitrogen molecule (nitrogen makes up around 4/5 of the air) at room temperature (293 K), we have

$$m = 28.0134 \text{ amu} = 4.65 \times 10^{-26} \text{ kg} \quad (8)$$

$$k = 1.38 \times 10^{-23} \text{ m}^2\text{kg s}^{-2}\text{K}^{-1} \quad (9)$$

$$v_{rms} = 510.7 \text{ m s}^{-1} \quad (10)$$

Example 2. Consider a gas containing hydrogen and oxygen molecules in thermal equilibrium. The ratio of their rms speeds is

$$\frac{v_H}{v_O} = \sqrt{\frac{m_O}{m_H}} = \sqrt{\frac{31.9988}{2.016}} = 3.984 \quad (11)$$

where the masses are in amu. The hydrogen molecules are moving about 4 times faster than the oxygen molecules.

Example 3. To separate the two naturally occurring isotopes of uranium ^{235}U and ^{238}U , the uranium is combined with fluorine to make uranium hexafluoride gas UF_6 . The two isotopes will result in different rms speeds for the two types of molecules. We have

$$m_{235} = 235.04 + 6 \times 18.998 \text{ amu} = 5.794 \times 10^{-25} \text{ kg} \quad (12)$$

$$m_{238} = 238.02891 + 6 \times 18.998 \text{ amu} = 5.843 \times 10^{-25} \text{ kg} \quad (13)$$

$$v_{235} = \sqrt{\frac{3k \times 293}{m_{235}}} = 144.692 \text{ m s}^{-1} \quad (14)$$

$$v_{238} = \sqrt{\frac{3k \times 293}{m_{238}}} = 144.084 \text{ m s}^{-1} \quad (15)$$

Thus the speed difference is quite small.

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