

The Equipartition Theorem

By Dr. Chicken

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Every atom in every gas phase molecule has three motional degrees of freedom available to it. This is a result of our living in a three dimensional universe; this is how we have to begin the analysis as it doesn't get more simple than this. The number of degrees of freedom adds together, thus, every molecule has a total of $3N$ spatial degrees of freedom available to it where N is the number of atoms in the molecule. Now it turns out if every atom in a molecule are moving in the same direction, that's just pure center-of-mass translation; ie. the molecule is banging against the walls. Since again we live in a 3D world, there are three purely translational degrees of freedom (x , y and z). Now for a linear molecule, the atoms may be moving in such a way that they are rotating; there are two ways to do this. For a non-linear molecule, there are three ways to rotate. While not entirely correct, you can think of the three rotations like a forward flip, a sideways somersault, and a pirouette (guys, your going to have to Google search "pirouette"). Thus, there are $3N-5$ (for linear molecules) and $3N-6$ (for non-linear molecules) degrees of motion left. These must be vibrations. Unfortunately, our terrestrial temperatures are too low to ever hope to vibrationally excite a molecule which is why they do not count towards the molecules internal energy (this is the same thing as saying I cannot "store" heat vibrationally). Let me re-create the chart I made on Friday for completeness:



A little known fact is that the Equipartition Theorem was discovered by this cute little donkey.

<u>Molecule</u>	<u>Degrees of Freedom</u>	<u>U</u>	<u>Terrestrial U</u>
Ar	3 translational	$3/2 k \cdot T$	$3/2 k \cdot T$
CO ₂	3 translational, 2 rotational, $3 \times 3 - 5 = 4$ vibrational	$9/2 k \cdot T$	$5/2 k \cdot T$
CH ₄	3 translational, 3 rotational, $3 \times 5 - 6 = 9$ vibrational	$15/2 k \cdot T$	$3 k \cdot T$