

Duane's Science Enrichment Series

The Ideal Gas Law - Three Derivations, One Reality

Keywords: Chemistry, Physics, Thermodynamics

Target: College General Chemistry

Your chemistry textbook talks about Charles' Law, Boyle's Law, and how they are joined into the Combined Gas Law:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} . \quad (I)$$

Therefore, we won't talk about that again here. It might go on to explain how this leads to the Ideal Gas Law. But it might not, so let's talk about that. It follows from (I) that either side of the equation must equal a constant.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = k \Rightarrow PV = kT . \quad (II)$$

Let's not get into what k is right now, but it follows further that it must depend upon the amount of gas, so we can write it again as the Ideal Gas Law:

$$PV = nRT . \quad (III)$$

We already know that n is the number of moles, and from that it is easy to calculate a value for the Rankine gas constant, R .

But there's another way.

The Ideal Gas Law from the Kinetic Theory of Gasses

Your book talks about this, too. The Kinetic Theory of Gasses stipulates some details such as the size of molecules being small compared to the volume they occupy, that for an ideal gas there are no intermolecular forces, that the average kinetic energy is proportional to temperature, and some other things that you can look up. Putting all this together with what you know about basic physics, one can derive an expression for pressure based on molecular mass and average velocity. We won't do that here because it's a couple more pages and you can look it up online. But the expression is

$$P = \frac{1}{3} \frac{N}{V} m\bar{v}^2 = \frac{1}{3} \frac{N}{V} 2K , \quad (IV)$$

where N is the number of particles, K is the average kinetic energy, and everything else is what you think they are. Recall that one of the premises of the Ideal Gas Law is that average kinetic energy is proportional to temperature, so we can rewrite (IV) as

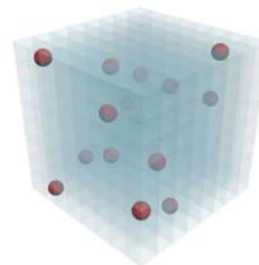
$$P = \frac{2}{3} \frac{N}{V} k_1T = \frac{N}{V} kT \Rightarrow PV = NkT = nRT . \quad (V)$$

The k here isn't exactly the same as the one in (II), but it's close and we'll talk more about this in just a moment. The point is that the Kinetic Theory of Gasses gives the same result as the combined gas law, which should not be surprising, because the behavior of the molecules in experiment is exactly what is described by the Kinetic Theory of Gasses. But now lets move to something completely different.

The Ideal Gas Law from Statistical Mechanics

Statistical mechanics is something that you run into in Physical Chemistry and might be slammed with again in graduate school. But it's really awesome. It's all about probabilities and how what you are most likely to observe is what's most likely. That should be obvious enough. But let's start at the beginning.

Let's discuss how probability fits into this by using a lattice model as shown to the right. We create a lattice of M volume elements V_0 filling a volume V and fill some of them with N particles. At first glance, this looks nothing like the Kinetic Theory of Gasses; the molecules aren't even moving. But the cool thing about lattice models in statistical mechanics, is that even when they are this simple, if you do the mathematics properly, they give the correct results. It's sort of like mathematical magic.



Now for that probability. The number of ways that you can arrange N particles into M slots is

$$W = \frac{M!}{(M-N)!N!}. \quad (\text{VI})$$

For a mole of gas molecules, this is a very, very large number. Think of a mole of moles, or maybe a mole of moles of moles. That large. But the beauty is that it doesn't really matter what that number is. If we assume that the number of molecules is very much less than the number of slots (one of the conditions of the Ideal Gas Law, remember?), then we can approximate this as

$$W \approx \frac{1}{N!} M^N = \frac{1}{N!} \left(\frac{V}{V_0} \right)^N. \quad (\text{VII})$$

It is cool to know that the man behind statistical mechanics is Stefan Boltzmann, and that the equation written on his tombstone, in the mathematical language of the day, is

$$S = k_B \ln W, \quad (\text{VIII})$$

which relates entropy S to the number of possible configurations. Substituting (VII) into (VIII) gives

$$S = k_B \ln \left(\frac{1}{N!} \left(\frac{V}{V_0} \right)^N \right) = k_B \ln \frac{1}{N!} + Nk_B \ln \left(\frac{V}{V_0} \right) = S_0 + Nk_B \ln \left(\frac{V}{V_0} \right), \quad (\text{IX})$$

Where S_0 is a base entropy that depends only on the number of molecules and is independent of the volume. Taking the partial derivative with respect to volume,

$$\frac{\partial S}{\partial V} = \frac{Nk_B}{V}. \quad (\text{X})$$

We know from classical thermodynamics that $\partial S / \partial V = P / T$, so we can substitute this into (X).

$$\frac{\partial S}{\partial V} = \frac{Nk_B}{V} = \frac{P}{T} \Rightarrow PV = Nk_B T = nRT. \quad (\text{XI})$$

If you didn't know that $Nk_B = nR$, this is a good time to find out. The Boltzmann constant k_B is related to the gas constant R by a factor of Avogadro's number. Work it out. This is also the time to bring up that all the other k 's in the equations above are really variations of k_B .

The Big Picture

But did you see what happened? We got exactly the same Ideal Gas Law using statistics and classical thermodynamics as we did from the Kinetic Theory of Gasses, using different simplifying assumptions.

Stop right there! Did we really use different assumptions? The Kinetic Theory assumption that particles are very small in relation to the space between them is really the same assumption as the statistical mechanical one that the number of particles is small compared to the number of volume elements. Both mean that the pressure is low.

What about the assumption that the average kinetic energy of molecules is proportional to temperature? We didn't talk about it here, but one of the principles of statistical mechanics is that at constant temperature and number of particles, the energy of the individual particles follows the *Boltzmann distribution*, and this is the very thing that makes the temperature/kinetic energy connection work out the way it does.

Here is the big picture encompassing all of this. The Kinetic Theory of Gasses and statistical mechanics give the same result because they are simply different ways of looking at the same underlying reality. If they didn't, there would be something wrong with nature, or at least with the models. Put another way, the kinetic model and the statistical model are the *same thing*.

I have issues with the way chemistry in particular and science in general are taught. They focus on little snapshots of reality and rarely take the time to put them together into the big picture. If you are serious about science, then take that time yourself, and look for the connections that put the pieces together. Here is a clue. Except for the Pauli exclusion principle and nuclear chemistry, everything in your general chemistry textbook is quantum mechanics and thermodynamics, and everything in thermodynamics can be written as the probabilities of statistical mechanics.