

1.1: Units and the Perfect Gas Law

We need a way to calculate how much a gas (n = moles) is pressurized (P) when we heat it (T = temperature in Kelvin), which depends on the size of the container (V = volume). A lot of people have already had this idea, so much so that in the late 1600's Robert Boyle among others noted that pressure is inversely proportional to volume. Despite the fact that Boyle was more of an "alchemist" compared to a modern-day scientist, he had particularly good measuring equipment as shown in Figure 1.1 and was able to correlate pressure to volume over a range of $4\times$ to demonstrate a near-perfect $P \propto \frac{1}{V}$ relationship. He used units of inches of mercury for the pressure because he used a mercury manometer for making measurements. It took another 200 years for Jacques Charles to discover that volume is proportional to temperature. He figured this out during his development of the first lighter-than-air balloon, having isolated hydrogen gas from the reaction of iron with acid. From there it took little time for Amedeo Avogadro to discover that, for gases at the same temperature and pressure, the gas's volumes are proportional to the gas's molecular weights. Most importantly he suggested that molecules are formed from atoms (this was new in the 1800's).

If we put this together we find:

$$PV \sim nT$$

but we have already run into a problem- the units are inconsistent! To see what we mean, let's start with pressure for which there are many units including inches of mercury, atmospheres, and bars. However, the standard S.I. unit of pressure is the Pascal, which is a Newton (a unit of force) per unit area (a meter squared, as the meter is the S.I. unit of length). Since a Newton is: $\frac{kg \cdot m}{s^2}$, then the Pascal is: $\frac{kg \cdot m}{s^2} \cdot \frac{1}{m^2} = \frac{kg}{s^2 \cdot m}$. When pressure is multiplied by volume in units of m^3 the result is in Joules: $PV = \frac{kg \cdot m^2}{s^2}$, which is energy. But nT is in units of mole·Kelvin, *which is not a Joule*. Thus, the equation: $PV \sim nT$ must be fixed to make the units work, which we will do by multiplying the right side by a constant "R" that simply divides out the mole·Kelvin and leaves energy behind as $\frac{J}{mol \cdot K}$:

$$PV = nRT \tag{1.1.1}$$

In the SI system the gas constant is specifically $R = 8.314 \frac{J}{mol \cdot K}$. Now we have Joules on the left and Joules on the right. In fact, this has to happen for every equation that describes a real system. There are three rules for the units of an equation:

1. The left and right sides of an equation must have the same units.
2. Terms in a sum must have the same units. For example, in the equation: $a \pm b = c$, "a" and "b" have the same units.
3. Terms in an equation multiply or divide into different units. Applying this to the above, term "c" has the inverse units of "a" and "b". Numbers like π or 2.0 have no units at all.

Getting back to task, does $PV = nRT$ look familiar? Of course! It is the perfect gas equation that you learned about in high school. Hence, we have an equation for solving the pressure generated by a hot gas, which we will use to calculate the energy of an expanding piston inside a car engine. But is $PV = nRT$ a "perfect" equation? I think not- and here is how you can tell. You are probably aware that molecules comprise the moles of gas in $PV = nRT$, and I wouldn't expect all gas molecules to behave the same way. For example, take water at room temperature and pressure. How can $PV = nRT$ be correct, after all water is a liquid! Here is a better example- trimethyl indium ($InMe_3$) can spontaneously explode in the gas phase, but I don't see that behavior in $PV = nRT$! Basically, the problem is that there is no input into the perfect gas equation for what the gas is which is clearly important, so the perfect gas law must be an approximation.

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