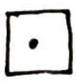
Boltzman Entropy

In the Joule Expansion, we saw that the gas freely expand in the way it does? The answer is simply, "because it can!" To quantify this we will define a new state variable : entropy.

Entropy is a quantity that track spontaneous changes. To understand it, we will first think about microstates. Microstates are a complete and perfect description of the configuration of a thermodynamic system. It would be impossible to count every possible configuration of particles of a gas in a vessel so let's simplify the problem a little.

Consider breaking space into very small cells such that if a particle is anywhere in this cell it counts as the same microstate. We will define a term multiplicity, Ω, to be the total number of microstates.


single particle in a cell of volume V_1 multiplicity $= \Omega_0$


single particle in extended volume V_2 multiplicity $= \Omega_0 \frac{V_2}{V_1} = \Omega_0'$


two particles in a volume V_1 multiplicity $= \Omega_0^2$


two particles in extended volume V_2 multiplicity $= (\Omega_0')^2 = \Omega_0^2 \left(\frac{V_2}{V_1}\right)^2$

So it should be convincing that N particles in a volume V_1 have multiplicity $\Omega_0^N = \Omega$ and N particles in an extended volume V_2 have multiplicity $(\Omega_0')^N = \Omega \left(\frac{V_2}{V_1}\right)^N = \Omega'$

We can now define entropy S, as Boltzmann did, as the natural log of the multiplicity of a system.

$$\boxed{S = k_B \ln(\Omega)}$$

It is virtually impossible to measure this however so will instead try to find ΔS, the change in entropy. For the free expansion (Joule Expansion) example:

$$\Delta S = k_B \ln(\Omega') - k_B \ln(\Omega)$$

These are the multiplicities for the V_1 and extended volume V_2 we previously worked out.

$$= k_B \ln\left(\frac{\Omega'}{\Omega}\right)$$

$$= k_B \ln\left(\frac{\Omega\left(\frac{V_2}{V_1}\right)^N}{\Omega}\right)$$

$$= k_B \ln\left(\frac{V_2}{V_1}\right)^N = \underline{\underline{N k_B \ln\left(\frac{V_2}{V_1}\right)}}$$

Entropy is a measure of disorder, conditions that allow less microstates (smaller volume or less particles), mean lower entropy since the system has more "order". Entropy is a state variable.

The total entropy of two systems together is the sum of their individual entropies.

Clausius Entropy ~

Let's go back to the isothermal expansion. Since this was a reversible process, we can track entropy change on an infinitesimal level. So consider the volume increasing from V to $V+dV$

$$\Delta S = k_B \ln(\Omega') - k_B \ln(\Omega)$$

$$dS = k_B \ln\left(\frac{\Omega'}{\Omega}\right) = k_B \ln\left(\frac{V_2}{V_1}\right)^N$$

$$\therefore dS = N k_B \ln\left(\frac{V+dV}{V}\right) = N k_B \ln\left(1 + \frac{dV}{V}\right)$$

If we do taylor expansion of $\ln\left(1+\frac{dV}{V}\right)$, keeping in mind $\frac{dV}{V} \ll 1$, we find $\ln\left(1+\frac{dV}{V}\right) \approx \frac{dV}{V}$

$$\therefore dS = \frac{N k_B \, dV}{V}$$

Now, using $PV = Nk_BT$

$$\frac{P}{T} = \frac{Nk_B}{V}$$

$$dS = \frac{P}{T} dV$$

and $P dV = -đW$

$$dS = \frac{-đW}{T}$$

since $dU = đQ + đW$ and $dU = 0$

$$đQ = -đW$$

So finally: $\boxed{dS = \frac{đQ}{T}}$ This is the definition of entropy for reversible processes.

For general, not necessarily reversible processes, we can say $dS \geq \frac{đQ}{T}$