

Boltzmann's Entropy Equation

The entropy and the number of microstates of a specific system are connected through the Boltzmann's entropy equation (1896):

$$S = k \ln W$$

2nd Law of

Thermodynamics:

$$\Delta S \geq 0$$

For a closed system, entropy can only increase, it can never decrease.

For an irreversible process the entropy increases.

For a reversible process the change in entropy is zero.

Some Definitions

The **configuration** of a system is some measurable state in which the system resides.

Example1: 6 molecules are distributed 4 on the left, 2 on the right.

Example2: A gas on n mole in a volume V has temperature T and pressure P.

The number of **microstates** for a configuration is the number of ways in which the configuration can be put together. This number of ways is called the **multiplicity**, W , of the configuration.

We find the number of microstates by "counting" them. There are mathematical methods for counting (combinatorics) that help us. The **factorial** ($N!$) is one such tool. $N!$ is the number of ways in which N items (particles, spin states) can be arranged. It is equal to: $N! = N * (N-1) * (N-2) \dots (2) * (1)$.

When counting microstates, we have to be careful to not count states twice (or more). Since usually we deal with molecules that can not be distinguished from each other (since they are identical) we need to make sure we divide out all the ways in which the molecules can be arranged in their state.

Some Examples.

Sixty particles in a box, no division between left and right. Then the number of microstates is:

$$W = \frac{60!}{60!} = 1$$

Ten particles in a box, with 2 distinct sides, so a particle is either on the left or on the right. We have 6 particles on the left, 4 on the right:

$$W = \frac{10!}{6!4!} = 210$$

Ten particles in a box, with 3 distinct regions, left, middle, right, filled with 5,3,2 particles resp.

$$W = \frac{10!}{5!3!2!} = 2520$$

One hundred particles in a box, 10 regions, each region has 10 particles:

$$W = \frac{100!}{(10!)^{10}} = 2.36 \cdot 10^{92}$$

Entropy - Thermodynamic View

Rudolf Clausius (1865):

Entropy is the amount of thermal energy put into a system that can not be extracted as work.

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

In a cyclic process, you can convert heat in to work (i.e. a steam engine). However, you can never convert all the heat fully into work, some of it is lost.

At constant temperature we have: $\Delta S = \frac{Q}{T}$

Entropy as State Function

If entropy is a state function, then the entropy of a system is the same whenever it is in the same state. Thus a cyclic process must have $\Delta S=0$.

For an ideal gas we can write down the change in entropy between 2 states as:

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) + nC_V \ln\left(\frac{T_f}{T_i}\right)$$

Engines

In a thermodynamic sense, engines turn heat into work. No engine can convert all the heat at the input into work, some heat must be discharged. Thus, an engine needs a hot reservoir for heat input, and a cold reservoir for heat output. You cannot extract work when you have no temperature difference.

Any Ideal Engine:

For any ideal engine we use a gas that does work in a cyclic process, each step of this process is reversible, thus for one full cycle, for the gas: $\Delta P=0$, $\Delta V=0$, $\Delta T=0$, $\Delta E_{\text{int}}=0$, $\Delta S=0$.

Carnot Engine

Ideal Carnot Engine:

In a Carnot Engine the gas absorbs heat during an isothermal expansion at T_H , then adiabatically expands to T_L , then releases heat during an isothermal contraction at T_L , and finally contracts further adiabatically to come back to the initial temperature T_H

Properties: $\Delta E_{\text{int}} = 0 \Rightarrow W = Q \Rightarrow W = |Q_H| - |Q_L|$

$$\Delta S = \Delta S_H + \Delta S_L = 0 \Rightarrow \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L} = 0 \Rightarrow \frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$$

$$\varepsilon_C = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H}$$