

Entropy of Mixing - Gibbs paradox

Consider two different gases (red and blue) at the same temperature and pressure, separated by a partition

E_1, V_1, N_1	E_2, V_2, N_2
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$$\left. \begin{aligned} V_1 + V_2 &= V \\ N_1 + N_2 &= N \\ E_1 + E_2 &= E \end{aligned} \right\} \text{constant}$$

both gases at same T and $p \Rightarrow \begin{cases} E_1 = \frac{3}{2} N_1 k_B T, & V_1 = N_1 k_B T / p \\ E_2 = \frac{3}{2} N_2 k_B T, & V_2 = N_2 k_B T / p \end{cases}$

With the partition in place, the total entropy is initially

$$S_i = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

Now remove the partition and let the gases mix. The temperature + pressure should not change. $\Rightarrow E_1$ and E_2 remain constant. Also N_1 and N_2 remain constant. The only changes are $V_1 \rightarrow V$ and $V_2 \rightarrow V$.

With the partition removed, the final entropy is

$$S_f(E, V, N_1, N_2) = k_B \ln [\Omega_1(E_1, V, N_1) \Omega_2(E_2, V, N_2)]$$

$$= S_1(E_1, V, N_1) + S_2(E_2, V, N_2)$$

The entropy of mixing is $\Delta S = S_f - S_i$

If we use our result for the ideal gas, we get

$$S_i = \frac{3}{2} k_B N_1 + k_B N_1 \ln \left[\frac{V_1}{h^3} \left(\frac{4}{3} \pi m_1 \frac{E_1}{N_1} \right)^{3/2} \right] \\ + \frac{3}{2} k_B N_2 + k_B N_2 \ln \left[\frac{V_2}{h^3} \left(\frac{4}{3} \pi m_2 \frac{E_2}{N_2} \right)^{3/2} \right]$$

and

$$S_f = \frac{3}{2} k_B N_1 + k_B N_1 \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m_1 \frac{E_1}{N_1} \right)^{3/2} \right] \\ + \frac{3}{2} k_B N_2 + k_B N_2 \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m_2 \frac{E_2}{N_2} \right)^{3/2} \right]$$

$$\Rightarrow \Delta S = k_B N_1 \ln \left(\frac{V}{V_1} \right) + k_B N_2 \ln \left(\frac{V}{V_2} \right)$$

or since $V_1 = N_1 k_B T / p$ and $V_2 = N_2 k_B T / p$

$$\Delta S = k_B N_1 \ln \left(\frac{N_1 + N_2}{N_1} \right) + k_B N_2 \ln \left(\frac{N_1 + N_2}{N_2} \right) > 0$$

We expect $\Delta S > 0$ since entropy increases when a constraint is removed.

When the red gas mixes with the blue gas we get purple gas! The process is irreversible - there is no thermodynamic way to separate back into separate volumes of blue and red gas. In irreversible processes, the entropy increases (this is just the thermodynamic definition of an irreversible process)

Now consider what happens if the two gases on either side of the partition were the same type (both red).

With the partition removed, the system is a single gas of $N = N_1 + N_2$ particles, with total energy $E = E_1 + E_2$, confined to a volume V . The final state entropy is

$$S_f = S(E, V, N)$$

$$= \frac{3}{2} k_B N + k_B N \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m \frac{E}{N} \right)^{3/2} \right]$$

$$= \frac{3}{2} k_B (N_1 + N_2) + k_B (N_1 + N_2) \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi \frac{3}{2} k_B T \right)^{3/2} \right]$$

$$\Rightarrow S_f = \frac{3}{2} k_B N_1 + k_B N_1 \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m \frac{E_1}{N_1} \right)^{3/2} \right]$$

$$+ \frac{3}{2} k_B N_2 + k_B N_2 \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m \frac{E_2}{N_2} \right)^{3/2} \right]$$

where we used $\frac{E}{N} = \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2} k_B T$.

$$\Rightarrow S_f = S(E, V, N) = S(E_1, V, N_1) + S(E_2, V, N_2)$$

[In general $S(E, V, N)$, instead of obeying the extensivity relation, obeys $\lambda S(E, V, N) = S(\lambda E, V, \lambda N)$, which is consistent with the above]

So S_f has exactly the same form when both gases are the same, as when they are different!

Hence we find the same $\Delta S > 0$, as when the gases were different! But this cannot be - when the gases are the same, removing the partition is a reversible process. We can always reinsert the partition and return to ~~the~~ a situation indistinguishable from the initial state. In such a reversible process, we should have $\Delta S = 0$!

The source of the problem lies in whether or not one should regard the particles of the gas as distinguishable. If we can distinguish each and every particle of the gas from one another, then when we mix two gases of the same type, we do not really have a reversible process. After the partition is reinserted, we have not returned to the initial state because we now have different particles on each side as compared to what was initially. Think of each particle as being a different color, and the point is clear. And if each particle is a different color (ie is distinguishable) it is no longer clear that the entropy should be extensive. If we double the volume, energy, and number of particles, we have not just made a second copy of the original system, since all the new particles must come in new colors!

It was Gibbs who realized that to resolve this paradox of the mixing entropy, as well as to make the entropy extensive, it was necessary to regard the particles of a gas as indistinguishable from one another. This assumption is verified by quantum mechanics.

Indistinguishable Particles

When the particles are indistinguishable, the state where particle 1 is at coordinates (q_1, p_1) and where particle 2 is at coordinates (q_2, p_2) is indistinguishable from the state where particle 1 is at (q_2, p_2) and 2 is at (q_1, p_1) .

In counting the number of states Ω we have therefore overcounted. The correct counting should be

$$\Omega(E, V, N) = \frac{1}{N!} \int \frac{dq_i \int dp_i}{h^{3N}} \\ E \leq H(q_i, p_i) \leq E + \Delta$$

$N!$ Since there are N ways to choose which particle is at coords (q_1, p_1) , $(N-1)$ ways to choose which of the remaining particles are at coords (q_2, p_2) , etc...

So our new ~~def~~ result for the entropy is related to our ~~old~~ old result by

$$S^{\text{new}} = S^{\text{old}} - k_B \ln N! = S^{\text{old}} - k_B N \ln N + N$$

where we used Stirling's formula $\ln N! = N \ln N - N$ for large N .

The new result for the entropy of an ideal gas is thus

$$S(E, V, N) = \frac{5}{2} k_B N + k_B N \ln \left[\frac{V}{h^3 N} \left(\frac{4}{3} \pi m \frac{E}{N} \right)^{3/2} \right] \quad \text{Sackur-Tetrode Egn.}$$

this result clearly gives an S that is now extensive and agrees with the result we got from integrating the Gibbs-Duhem relation.

$$\left[\begin{array}{l} \text{We now have } \lambda S(E, V, N) = S(\lambda E, \lambda V, \lambda N) \text{ rather} \\ \text{than the old result } \lambda S(E, V, N) = S(\lambda E, V, \lambda N) \end{array} \right]$$

Considering the entropy of mixing, our earlier result remains unchanged if the two gases are different types.

But if the two gases are the same type, we now have

$$S_f = S(E, V, N) = \frac{5}{2} k_B N + k_B N \ln \left[\frac{V}{h^3 N} \left(\frac{4}{3} \pi m \frac{E}{N} \right)^{3/2} \right]$$

$$S_i = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

$$= \frac{5}{2} k_B (N_1 + N_2) + k_B N_1 \ln \left[\frac{V_1}{h^3 N_1} \left(\frac{4}{3} \pi m \frac{E_1}{N_1} \right)^{3/2} \right] + k_B N_2 \ln \left[\frac{V_2}{h^3 N_2} \left(\frac{4}{3} \pi m \frac{E_2}{N_2} \right)^{3/2} \right]$$

$$\text{Using } \frac{E}{N} = \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2} k_B T \text{ we get}$$

$$\begin{aligned} \Delta S = S_f - S_i &= k_B N \ln \left(\frac{V}{N} \right) - k_B N_1 \ln \left(\frac{V_1}{N_1} \right) - k_B N_2 \ln \left(\frac{V_2}{N_2} \right) \\ &= k_B N_1 \ln \left(\frac{V N_1}{V_1 N} \right) + k_B N_2 \ln \left(\frac{V N_2}{N V_2} \right) \end{aligned}$$

But using $V = N k_B T / p$, $V_1 = N_1 k_B T / p$, $V_2 = N_2 k_B T / p$

we get $\frac{V}{V_1} = \frac{N}{N_1}$, $\frac{V}{V_2} = \frac{N}{N_2}$ so

$$\Delta S = k_B N_1 \ln \left(\frac{N}{N_1} \frac{N_1}{N} \right) + k_B N_2 \ln \left(\frac{N}{N_2} \frac{N_2}{N} \right)$$

$$= k_B N_1 \ln(1) + k_B N_2 \ln(1) = 0$$

entropy of mixing = 0 as desired!

Note: If one has N_1 particles of one type of gas, and N_2 particles of a different type of gas, in the same box of volume V , we have

$$S(E, V, N_1, N_2) = S_1(E_1, V, N_1) + S_2(E_2, V, N_2)$$

(where E_1 and E_2 must be such that the temperatures are equal)

But if both gases are the same (ie we have only mentally divided them up into one group of N_1 and another of N_2) then it is NOT true that

$$S(E, V, N) = S(E_1, V, N_1) + S(E_2, V, N_2)$$

This will not be true because the particles are indistinguishable. This cannot be true if

S is extensive — because $S(E, V, N) \neq 2S(\frac{E}{2}, V, \frac{N}{2})$,

~~but~~ as the above would imply, but rather

$$S(E, V, N) = 2S(\frac{E}{2}, \frac{V}{2}, \frac{N}{2}) !$$

Canonical Ensemble

Consider a system of interest in contact with a thermal reservoir - ie system is separated from reservoir by a fixed impenetrable but thermally conducting wall. Let E be the energy of the system, and $E_T - E$ be the energy of the reservoir. Total energy E_T is fixed. Then

$$\Omega_T(E_T) = \int \frac{dE}{\Delta} \underbrace{\Omega(E)}_{\text{system}} \underbrace{\Omega_R(E_T - E)}_{\text{reservoir}}$$

The prob that the system has energy E is therefore

$$P(E) \propto \Omega(E) \Omega_R(E_T - E) = \Omega(E) e^{S_R(E_T - E)/k_B}$$

Since the reservoir is large, $E \ll E_T$, so we can expand

$$\begin{aligned} \Omega_R(E_T - E) &\approx \exp \frac{1}{k_B} \left\{ S_R(E_T) - \frac{\partial S_R}{\partial E_R}(E) + \dots \right\} \\ &= \exp \frac{1}{k_B} \left\{ S_R(E_T) - \frac{E}{T} \right\} = \text{const} e^{-E/k_B T} \end{aligned}$$

$$\text{So } P(E) \propto \Omega(E) e^{-E/k_B T} = e^{S(E)/k_B - E/k_B T} = e^{-A}$$

$$\Rightarrow \boxed{P(E) = \frac{\Omega(E) e^{-E/k_B T}}{\Delta Q_N(T, V)}} \quad \text{normalization} \quad \int dE P(E) = 1$$

where

$$\boxed{Q_N(T, V) = \int \frac{dE}{\Delta} \Omega(E) e^{-E/k_B T}} \quad \text{is the canonical partition function}$$

$$\text{if energy levels are discrete } Q_N(T, V) = \sum_{E_i} \Omega(E_i) e^{-E_i/k_B T}$$

$$\text{or } Q_N(T, V) = \frac{1}{N!} \frac{1}{h^{3N}} \int dq_i dp_i e^{-H(q_i, p_i)/k_B T}$$

Note: In the canonical ensemble, the energy of the system of interest ~~is not fixed~~ is not fixed, but follows a probability distribution set by a fixed temperature. The temperature determines the average energy. Canonical ensemble does not depend on any details of the reservoir.

We saw in thermodynamics that when one wishes to use T as the variable rather than S , the potential to use is the Helmholtz free energy $A(T, V, N)$. We now see that there is a direct relation between A and the canonical ensemble.

First note that the average energy in canonical ensembles is:

$$\langle E \rangle = \int \frac{dE}{\Delta} E p(E) = \frac{\int \frac{dE}{\Delta} E \Omega(E) e^{-E/k_B T}}{\int \frac{dE}{\Delta} \Omega(E) e^{-E/k_B T}}$$

$$\text{let } \boxed{\beta = 1/k_B T}$$

$$\langle E \rangle = \frac{-\frac{\partial}{\partial \beta} \left[\int \frac{dE}{\Delta} \Omega(E) e^{-\beta E} \right]}{\int \frac{dE}{\Delta} \Omega(E) e^{-\beta E}} = -\frac{\partial}{\partial \beta} \ln \left[\int \frac{dE}{\Delta} \Omega(E) e^{-\beta E} \right]$$

$$\boxed{\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q_N(T, V)}$$

$\langle \dots \rangle$ denotes average value