The Gibbs Paradox and the Entropy of Mixing

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1 The Setup: Mixing Two Gases

Imagine a rigid, thermally insulated box divided into two equal compartments by a removable partition.

- **Left compartment:** Contains N molecules of Gas A at volume V and temperature T.
- **Right compartment:** Contains N molecules of Gas B at volume V and temperature T.

When the partition is removed, the gases spontaneously mix. We want to calculate the change in the total entropy of the system, $\Delta S = S_{\text{final}} - S_{\text{initial}}$.

2 The Naive Classical Approach (The Paradox)

Before the integration of quantum mechanical concepts, the classical entropy of an ideal gas was derived by integrating over phase space without accounting for particle indistinguishability. This yields a "naive" entropy equation of the form:

$$S_{\text{naive}}(N, V, T) = N k_B \ln(V) + N f(T) \tag{1}$$

where $f(T)$ is a function of temperature alone. Let us calculate the mixing entropy using this formula.

2.1 Calculating the Entropy Change

Initial State: Before the partition is removed, the total entropy is simply the sum of the entropies of the two separate compartments:

$$S_{\text{initial}} = S_{\text{naive}}(N, V, T)_A + S_{\text{naive}}(N, V, T)_B = 2N k_B \ln(V) + 2N f(T) \tag{2}$$

Final State: After the partition is removed, each gas expands to fill the entire available volume, $2V$.

$$S_{\text{final}} = S_{\text{naive}}(N, 2V, T)_A + S_{\text{naive}}(N, 2V, T)_B = 2N k_B \ln(2V) + 2N f(T) \tag{3}$$

The Entropy Change (ΔS):

$$\begin{aligned}
\Delta S_{\text{naive}} &= S_{\text{final}} - S_{\text{initial}} \\
&= 2N k_B \ln(2V) - 2N k_B \ln(V) \\
&= 2N k_B \ln\left(\frac{2V}{V}\right)
\end{aligned}$$

$$\Delta S_{\text{naive}} = 2N k_B \ln(2) \tag{4}$$

2.2 The Contradiction

If Gas A and Gas B are chemically distinct (e.g., Helium and Argon), this result makes perfect thermodynamic sense. The mixing is an irreversible process, and therefore $\Delta S > 0$.

However, what if Gas A and Gas B are the *exact same gas* (e.g., both are Helium)? Removing the partition changes absolutely nothing about the macroscopic state of the system. Reinserting the partition restores the exact original state without any work being done. The process is completely reversible, meaning ΔS must strictly be 0. Yet, the classical formula still predicts an increase of $2Nk_B \ln(2)$. This glaring contradiction is known as the **Gibbs Paradox**.

3 The Resolution: Particle Indistinguishability

The paradox is resolved by recognizing a fundamental quantum mechanical reality: identical particles are indistinguishable. In the classical phase space integral, swapping the positions and momenta of two identical Helium atoms does not create a new, distinct physical microstate.

To correct the overcounting of states, we must introduce a factor of $1/N!$ into the multiplicity (and thus the partition function). Applying Stirling's approximation ($\ln N! \approx N \ln N - N$) to this term modifies the volume dependence in the entropy equation from an extensive variable V to an intensive density ratio V/N. This gives us the **Sackur-Tetrode equation**:

$$S = Nk_B \left[\ln \left(\frac{V}{N\lambda_Q^3} \right) + \frac{5}{2} \right] \tag{5}$$

where λ_Q is the thermal de Broglie wavelength.

4 Proof: Mixing Identical vs. Distinguishable Gases

Let us apply the correct Sackur-Tetrode equation to both mixing scenarios to demonstrate the resolution. To simplify the notation, let $C = \frac{e^{5/2}}{\lambda_Q^3}$, allowing us to write the entropy as $S = Nk_B \ln\left(\frac{V}{N}C\right)$.

4.1 Scenario A: Mixing Identical Gases

Assume both compartments contain identical molecules (e.g., Helium).

Initial State: Two separate compartments, each with N particles and volume V.

$$S_{\text{initial}} = S_{\text{left}} + S_{\text{right}} = Nk_B \ln\left(\frac{V}{N}C\right) + Nk_B \ln\left(\frac{V}{N}C\right) = 2Nk_B \ln\left(\frac{V}{N}C\right) \tag{6}$$

Final State: We now have a single continuous system with $2N$ particles occupying a total volume of $2V$.

$$S_{\text{final}} = (2N)k_B \ln\left(\frac{2V}{2N}C\right) = 2Nk_B \ln\left(\frac{V}{N}C\right) \tag{7}$$

Change in Entropy:

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = 0 \tag{8}$$

The Sackur-Tetrode equation correctly predicts that mixing identical gases produces no increase in entropy.

4.2 Scenario B: Mixing Distinguishable Gases

Assume the left compartment contains Helium (Gas A) and the right contains Argon (Gas B). Because the particles are distinguishable, they must be treated as two separate interpenetrating systems that happen to share the same volume.

Initial State:

$$S_{\text{initial}} = S_A(N,V) + S_B(N,V) = Nk_B \ln\left(\frac{V}{N}C_A\right) + Nk_B \ln\left(\frac{V}{N}C_B\right) \tag{9}$$

Final State: Gas A expands to volume $2V$ (but still only contains N particles of type A). Gas B also expands to volume $2V$ (with N particles of type B).

$$S_{\text{final}} = S_A(N,2V) + S_B(N,2V) = Nk_B \ln\left(\frac{2V}{N}C_A\right) + Nk_B \ln\left(\frac{2V}{N}C_B\right) \tag{10}$$

Change in Entropy:

$$\begin{aligned}
\Delta S &= S_{\text{final}} - S_{\text{initial}} \\
&= Nk_B \left[\ln\left(\frac{2V}{N}C_A\right) - \ln\left(\frac{V}{N}C_A\right)\right] + Nk_B \left[\ln\left(\frac{2V}{N}C_B\right) - \ln\left(\frac{V}{N}C_B\right)\right] \\
&= Nk_B \ln\left(\frac{2V/N}{V/N}\right) + Nk_B \ln\left(\frac{2V/N}{V/N}\right) \\
&= Nk_B \ln(2) + Nk_B \ln(2)
\end{aligned}$$

$$\Delta S = 2Nk_B \ln(2) \tag{11}$$

The entropy of mixing for distinguishable gases remains strictly positive, perfectly aligning with the thermodynamic reality of irreversible mixing.