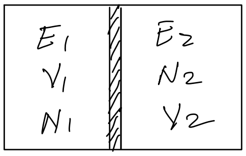
Unit 2-6: Entropy of Mixing and the Gibbs Paradox

Consider two different gases (red gas and blue gas) at the *same* temperature and pressure, separated by a partition. The total volume V, total number of particles N, and total energy E are all fixed to be constant. The exterior walls of the box are thermally insulating.



$$\left.\begin{aligned} V &= V_1 + V_2 \\ N &= N_1 + N_2 \\ E &= E_1 + E_2 \end{aligned}\right\} \text{constant} \tag{2.6.1}$$

Since both gases are at the same T and p we have,

$$E_1 = \frac{3}{2} N_1 k_B T, \qquad V_1 = \frac{N_1 k_B T}{p} \tag{2.6.2}$$

$$E_2 = \frac{3}{2} N_2 k_B T, \qquad V_2 = \frac{N_2 k_B T}{p} \tag{2.6.3}$$

With the partition in place, the total entropy is initially,

$$S_{\text{init}} = k_B \ln\left[\Omega_1(E_1, V_1, N_1)\Omega_2(E_2, V_2, N_1)\right] = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \tag{2.6.4}$$

Now we remove the partition and let the two gases mix. Clearly the number of particles in each gas, N_1 and N_2, do not change. We can also show that the temperature T of the gas does not change. This is because initially the total energy $E = E_1 + E_2 = (3/2)N_1 k_B T + (3/2)N_2 k_B T$. If the temperature after removing the partition was T', then the final energy would be $E' = (3/2)N_1 k_B T' + (3/2)N_2 k_B T'$. But since the exterior walls of the box are thermally insulating, the total energy is conserved, i.e. $E = E'$, and so we must have $T' = T$. The only changes are $V_1 \to V$ and $V_2 \to V$. With the partition removed, when the system comes into equilibrium the final entropy is,

$$S_{\text{final}}(E, V, N_1, N_1) = k_B \ln\left[\Omega_1(E_1, V, N_1)\Omega_2(E_2, V, N_2)\right] = S_1(E_1, V, N_1) + S_2(E_2, V, N_2) \tag{2.6.5}$$

The *entropy of mixing* is

$$\Delta S = S_{\text{final}} - S_{\text{init}} \tag{2.6.6}$$

If we use our result for the entropy of the ideal gas, computed from the microcanonical ensemble of the last section, we get,

$$S_{\text{init}} = \frac{3}{2} k_B N_1 + k_B N_1 \ln\left[\frac{V_1}{h^3}\left(\frac{4\pi m_1 E_1}{3N_1}\right)^{3/2}\right] + \frac{3}{2} k_B N_2 + k_B N_2 \ln\left[\frac{V_2}{h^3}\left(\frac{4\pi m_2 E_2}{3N_2}\right)^{3/2}\right] \tag{2.6.7}$$

and

$$S_{\text{final}} = \frac{3}{2} k_B N_1 + k_B N_1 \ln\left[\frac{V}{h^3}\left(\frac{4\pi m_1 E_1}{3N_1}\right)^{3/2}\right] + \frac{3}{2} k_B N_2 + k_B N_2 \ln\left[\frac{V}{h^3}\left(\frac{4\pi m_2 E_2}{3N_2}\right)^{3/2}\right] \tag{2.6.8}$$

We thus get

$$\Delta S = k_B N_1 \ln\left(\frac{V}{V_1}\right) + k_B N_2 \ln\left(\frac{V}{V_2}\right) \tag{2.6.9}$$

Now since $V_1 = N_1 k_B T/p$, $V_2 = N_2 k_B T/p$, and so $V = V_1 + V_2 = (N_1 + N_2)k_B T/p = N k_B T/p$, this can be written as,

$$\Delta S = k_B N_1 \ln\left(\frac{N_1 + N_2}{N_1}\right) + k_B N_2 \ln\left(\frac{N_1 + N_2}{N_2}\right) > 0 \tag{2.6.10}$$

We expect $\Delta S > 0$ since the entropy always 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 process that will separate the mixture back into separate volumes of red and blue gas. In irreversible processes, the entropy always increases.

Now consider what happens if the two gases on either side of the partition are both of the same type, say both are red gas. Before the partition is removed S_{init} is the same as in Eq. (2.6.7) except with $m_1 = m_2 = m$.
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 entropy with the partition removed is then,

$$S_{\text{final}} = S(E, V, N) = \frac{3}{2} k_B N + k_B N \ln\left[\frac{V}{h^3}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] \tag{2.6.11}$$

$$= \frac{3}{2} k_B (N_1 + N_2) + k_B (N_1 + N_2) \ln\left[\frac{V}{h^3}\left(\frac{4\pi m}{3}\, \frac{3}{2} k_B T\right)^{3/2}\right] \tag{2.6.12}$$

where we used $E/N = \frac{3}{2} k_B T$. Similarly using $E_1/N_1 = E_1/N_2 = \frac{3}{2} k_B T$ (since both sides were initially at the same temperature T), we can write the above as,

$$S_{\text{final}} = \frac{3}{2} k_B N_1 + k_B N_1 \ln\left[\frac{V}{h^3}\left(\frac{4\pi m}{3}\, \frac{E_1}{N_1}\right)^{3/2}\right] + \frac{3}{2} k_B N_2 + k_B N_2 \ln\left[\frac{V}{h^3}\left(\frac{4\pi m}{3}\, \frac{E_2}{N_2}\right)^{3/2}\right] \tag{2.6.13}$$

$$= S(E_1, V, N_1) + S(E_2, V, N_2) \tag{2.6.14}$$

We thus conclude that

$$S(E, V, N) = S(E_1, V, N_1) + S(E_2, V, N_2) \tag{2.6.15}$$

The above result is equivalent to our earlier observation that the entropy, as we've computed in the microcanonical ensemble so far, is not extensive. Rather than obeying the extensivity condition (i) $\lambda S(E, V, N) = S(\lambda E, \lambda V, \lambda N)$, we found that the entropy computed from the microcanonical ensemble obeyed (ii) $\lambda S(E, V, N) = S(\lambda E, V, \lambda N)$. If we took our initial gases so that $E_1 = E_2 = E/2$ and $N_1 = N_2 = N/2$, then Eq. (2.6.15) is equivalent to (ii) with $\lambda = 1/2$.

Comparing the above Eq. (2.6.13) with the previous Eq. (2.6.8), we see that S_{final} has exactly the same form when both gases are the same as when they are different, except with $m_1 = m_2 = m$.

Hence we find the same entropy of mixing $\Delta S > 0$ regardless of whether the two gases are the same or whether they are different! But this should not be – when the gases are the same, removing the partition is a *reversible* process. We can always reinsert the partition and return to a situation indistinguishable from the initial state. In such a reversible process we should have $\Delta S = 0$! This contradiction is known as the *Gibbs paradox* for the entropy of mixing.

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 the 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 the case initially.

Think of each particle as being a different unique color and the point should be clear. If each particle is a different color (i.e. the particles are distinguishable) it is no longer clear that the entropy should be extensive (or equivalently, additive over subsystems). If we double the volume, energy, and number of particles, we have not just made a second copy of the original system – this is because all the new particles must now 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 computed in the microcanonical ensemble extensive, it was necessary to regard the particles of a gas as being *indistinguishable* from one another. This assumption was later confirmed by our quantum mechanical understanding of atoms and molecules.

Note, above we showed that the temperature of the gas remains the same after the partition is removed. We can show that the pressure also remains the same.

When the two gases are *different* (red and blue), then Eq. (2.6.5) shows that

$$\frac{p'}{T} = \left(\frac{\partial S_{\text{final}}}{\partial V}\right)_{E,N_1,N_2} = \left(\frac{\partial S_1}{\partial V}\right)_{E_1,N_1} + \left(\frac{\partial S_2}{\partial V}\right)_{E_2,N_2} = \frac{p_1'}{T} + \frac{p_2'}{T} \tag{2.6.16}$$

so

$$p' = p_1' + p_2' \tag{2.6.17}$$

and the total pressure p' is the sum of the *partial pressures* p_1' and p_2' of each gas. But since we have an ideal gas, and the temperature does not change when the partition is removed ($T' = T$), then

$$p' = p_1' + p_2' = \frac{N_1 k_B T}{V} + \frac{N_2 k_B T}{V} = (N_1 + N_2)\frac{k_B T}{V} = \frac{N k_B T}{V} \tag{2.6.18}$$

But from the line preceding Eq. (2.6.10) we know that $N_1/V_1 = N_2/V_2 = N/V = p/k_BT$, i.e. the densities of the two gases before the partition was removed were equal, and this is the same as the total density of particles after the partition is removed. Therefore we conclude,

$$p' = p_1' + p_2' = p \tag{2.6.19}$$

The partial pressure of each component of the mixed gas decreases, but the total pressure remains constant.

When the two gases are the same (red and red), then we can apply the ideal gas law directly to the final mixture of $N = N_1 + N_2$ particles of red gas to conclude,

$$p' = \frac{N k_B T}{V} = \frac{N_1 k_B T}{V_1} = p \tag{2.6.20}$$

Again, the pressure does not change.