5.3 Thought experiment: Gibbs paradox

The result of Eq. (5.5) holds independent of the nature of the molecules, i.e. $\Delta_{mix} S_2^{id} = -\sum_i n_i R \ln x_i > 0$. So we can apply this equation on identical ideal gases (same p, T) for the step from state 1 to state 2 in Fig. 5.2 and expect an increase $\Delta S_{1-2} = \Delta_{mix} S$ larger zero.
We have a closed system and thus can separate the identical ideal gases reversibly in a second step, i.e. $\Delta S_{1-3} = 0$. Now state 1 and state 3 are identical and since S is a state function dS must be zero in disagreement to $\Delta S_{1-2} > 0$.

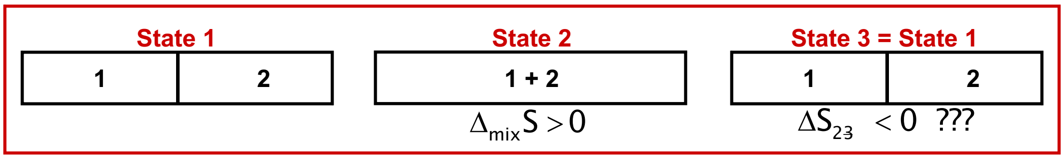

Figure 5.2: Illustration of the Gibbs paradox.

As we will see in TdK II the solution to this paradox is that the above discussed classical approach only holds for distinguishable particles, however, identical particles can not be distinguished! A full understanding needs a quantum mechanical description of the particles and translates into a change in the phase space volume:

$$\text{Distinguishable} \quad S \propto N \ln V \quad \rightarrow \quad S \propto N \ln \frac{V}{N} \quad \text{Indistinguishable} \tag{5.7}$$