

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  $\Omega$  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 ~~defn~~ result for the entropy is related to our ~~old~~ old result by

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

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

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

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

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

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

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

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

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

$$\text{(use } N = N_1 + N_2) \quad = k_B N_1 \ln \left( \frac{V N_1}{V_1 N} \right) + k_B N_2 \ln \left( \frac{V N_2}{N V_2} \right)$$

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

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

Consider the total number of states available to a system composed of the mixture of two gas with  $N_1$  and  $N_2$  particles respectively.

If the two gases are different types, i.e. red and blue, so that the particles of gas 1 can be distinguished from the particles of gas 2, then

$$\Omega_T(E, V, N_1, N_2) = \int_0^E \frac{d\bar{E}_1}{\Delta} \Omega_1(\bar{E}_1, V, N_1) \Omega_2(E - \bar{E}_1, V, N_2)$$

$\uparrow$  # states available to particles in gas 1       $\uparrow$  # states available to particles in gas 2

We already noted that the integrand will be strongly peaked about some particular  $\bar{E}_1$ , so

$$\Omega_T(E, V, N_1, N_2) \approx \Omega_1(\bar{E}_1, V, N_1) \Omega_2(E - \bar{E}_1, V, N_2)$$

and then

$$S_T(E, V, N_1, N_2) = S_1(\bar{E}_1, V, N_1) + S_2(E - \bar{E}_1, V, N_2)$$

$$\text{where } \left. \frac{\partial S_1}{\partial \bar{E}_1} \right|_{\bar{E}_1 = \bar{E}_1} = \left. \frac{\partial S_2}{\partial \bar{E}_2} \right|_{\bar{E}_2 = E - \bar{E}_1}$$

Now suppose the two gases are the same type, i.e. red and red, so that the particles of gas 1 cannot be distinguished from the particles of gas 2, then

$$\Omega_T(E, V, N_1, N_2) = \int_0^E \frac{dE_1}{\Delta} \frac{N_1! \Omega_1(E_1, V, N_1) N_2! \Omega_2(E_2, V, N_2)}{N!}$$

Here the factor  $\frac{N_1! N_2!}{N!}$  appears in the integrand

because of the indistinguishability of the two gases  
 i.e.  $N_1! \Omega_1(E_1, V, N_1)$  is the number of distinguishable states available to  $N_1$  red particles with energy  $E_1$   
 $N_2! \Omega_2(E_2, V, N_2)$  is the number of distinguishable states available to  $N_2$  red particles with energy  $E_2$

$\Rightarrow N_1! \Omega_1(E_1, V, N_1) N_2! \Omega_2(E_2, V, N_2)$  is the number of states available to the combined system with energy distributed into  $E_1$  and  $E_2$  if all particles are distinguishable

But since particles are indistinguishable the number of these states is really

$$\frac{N_1! \Omega_1(E_1, V, N_1) N_2! \Omega_2(E_2, V, N_2)}{N!}$$

Now the integral about  $E_1$  is strongly peaked about  $\bar{E}_1$ , so

$$\Omega_T(E, V, N_1, N_2) = \frac{N_1! N_2!}{N!} \Omega_1(\bar{E}_1, V, N_1) \Omega_2(\bar{E}_2, V, N_2)$$

$$S_T(E, V, N_1, N_2) = S_1(\bar{E}_1, V, N_1) + S_2(\bar{E}_2, V, N_2)$$

$$-k_B \ln \left( \frac{N!}{N_1! N_2!} \right)$$

using Stirling's approx, the last term is

$$\begin{aligned} \ln \frac{N!}{N_1! N_2!} &\approx N \ln N - N - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2 \\ &= N_1 \ln \left( \frac{N}{N_1} \right) + N_2 \ln \left( \frac{N}{N_2} \right) \end{aligned}$$

$$\text{as } N_1 + N_2 = N$$

So if  $S_{\text{same}}$  is entropy when the mixed gases are the same (red + red) and  $S_{\text{diff}}$  is the entropy when the mixed gases are different (red + blue) then

$$S_{\text{same}} = S_{\text{diff}} - k_B N_1 \ln \left( \frac{N}{N_1} \right) - k_B N_2 \ln \left( \frac{N}{N_2} \right)$$

$$= S_{\text{diff}} - \Delta S_{\text{diff}} \text{ where } \Delta S_{\text{diff}} \text{ was the entropy of mixing when the gases were different}$$

$$\text{Since } S_{\text{same}} = S_{\text{diff}}$$

$$\Rightarrow \Delta S_{\text{same}} = \Delta S_{\text{diff}} - \Delta S_{\text{diff}} = 0$$



## Canonical Ensemble

Consider a system of interest in contact with a thermal reservoir - a system is separated from reservoir by a fixed impermeable 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

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

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

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

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

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

Using the density of states

$$g(E) = \frac{1}{N!} \int \frac{dg_i}{h^{3N}} \int dp_i \delta(H(q_i, p_i) - E)$$

↑ Gibbs correction due to indistinguishable particles

$$\Omega(E) = g(E)\Delta$$

Then 
$$Q_N(T, V) = \int dE g(E) e^{-E/k_B T}$$

Probability 
$$P(E) = \frac{g(E) e^{-E/k_B T}}{Q_N(T, V)}$$

Combining the above

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

Boltzmann factor  $e^{-H/k_B T}$

The density of states  $g(E)$  has built into it all the information about a system as far as its thermodynamic behavior is concerned.

If one knows  $g(E)$ , then one can compute

the entropy 
$$S(E) = k_B \ln \Omega(E) = k_B \ln [g(E)\Delta]$$

Or one can compute the canonical partition function

$$Q_N(T, V) = \int dE g(E) e^{-E/k_B T}$$