Ideal gas

we had $\Omega(E,V,N) = \dfrac{V^N (2\pi m E)^{3N/2}}{h^{3N}\left(\frac{3N}{2}-1\right)!}\,\dfrac{\Delta}{E}$

for large N we use Stirling's formula $\ln N! \simeq N\ln N - N$

$S(E,V,N) = k_B \ln \Omega(E,V,N)$

$$= k_B \left\{ N \ln\left[\frac{V(2\pi m E)^{3/2}}{h^3}\right] - \left(\frac{3N}{2}-1\right)\ln\left(\frac{3N}{2}-1\right) + \left(\frac{3N}{2}-1\right) + \ln\frac{\Delta}{E} \right\}$$

use $\ln\left(\frac{3N}{2}-1\right) \simeq \ln \frac{3N}{2}\left(1-\frac{2}{3N}\right)$

$= \ln\frac{3N}{2} + \ln\left(1-\frac{2}{3N}\right)$

$\simeq \ln\frac{3N}{2} - \frac{2}{3N}$ expanding the log

$$S \simeq k_B \left\{ N\ln\left[\frac{V(2\pi m E)^{3/2}}{h^3}\right] - \frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2}\left(\frac{2}{3N}\right) + \ln\frac{3N}{2} - \frac{2}{3N} + \frac{3N}{2} - 1 + \ln\frac{\Delta}{E} \right\}$$

$\Delta \sim \frac{E}{N}$

$$= k_B \left\{ N \ln\left[\frac{V}{h^3}\left(\frac{2\pi m E}{\frac{3N}{2}}\right)^{3/2}\right] + \frac{3N}{2} + \ln\frac{3N}{2} + O\left(\frac{1}{N}\right) + \ln\frac{\Delta}{E} \right\}$$

as $N \to \infty$ leading terms are

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

(since the terms $\ln\frac{3N}{2} + \ln \Delta/E$ are negligible)

Note: since we took Δ so that

$$\frac{E}{N} < \Delta \ll E$$

then $$-\ln N < \ln \frac{\Delta}{E} \ll 0$$

or $\left|\ln \frac{\Delta}{E}\right| < \ln N$ is of order $\ln N$ and so can be ignored compared to terms of order N

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

note, our result does not depend on Δ, as we desired.

with the above, we recover the expected

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{\partial}{\partial E}\left(N k_B \frac{3}{2} \ln E \right) = \frac{3}{2} N k_B \frac{1}{E}$$

$$\Rightarrow \quad E = \frac{3}{2} N k_B T$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{\partial}{\partial V}\left(N k_B \ln V \right) = N k_B \frac{1}{V}$$

$$\Rightarrow \quad pV = N k_B T$$

so far so good!

But there is a problem – S above is <u>not</u> extensive. If we take $E \to 2E$, $V \to 2V$, $N \to 2N$, we do <u>not</u> get $S \to 2S$.

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

the $\ln V$ term in above spoils the desired extensivity

Compare the above to our earlier result for the ideal gas, obtained from combining $pV = Nk_BT$ and $E = \frac{3}{2}Nk_BT$ with the Gibbs-Duhem relation

(2) $$S(E,V,N) = \frac{N}{N_0} S_0 + k_B N \ln\left[\left(\frac{V}{V_0}\right)\left(\frac{E}{E_0}\right)^{3/2}\left(\frac{N}{N_0}\right)^{-5/2}\right]$$

this version is extensive – it scales proportionate to N. here V_0, E_0, N_0 constants. we have an extra factor N^{-1} in the log

Note: the Gibbs-Duhem relation was derived assuming S was extensive. Hence it should not be surprising that our expression (2) for S is extensive.

What is the physical reason why the expression (1) fails to be extensive?

$S(E,V,N)$ given in (1) does not obey the additive over subsystems behavior that we find in (2)

For (1) we do not have

$$\lambda S(E,V,N) = S(\lambda E, \lambda V, \lambda N)$$

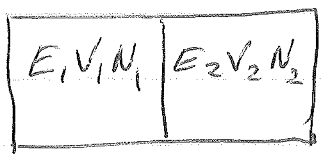
as we should. Rather (1) obeys

$$\lambda S(E,V,N) = S(\lambda E, V, \lambda N)$$

What is the source of this problem?

Entropy of Mixing – Gibbs paradox

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



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

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 and N_1 and N_2 should not change. $\Rightarrow$ E_1 and E_2 remain constant. ~~Also N_1 and N_2 remain constant~~. The only changes are $V_1 \to V$ and $V_2 \to V$.

With the partition removed, the final entropy is

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

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

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 $V_2 = N_2 k_B T/p$ $\quad V = V_1 + V_2$

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

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

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

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

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

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

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

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

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

[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 computing the number of states Ω we have therefore over counted. The correct counting should be

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

$N!$ 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 ~~defin~~ result for the entropy is related to our ~~odd~~ old result by

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

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

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

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

[We now have $\lambda S(E,V,N) = S(\lambda E, \lambda V, \lambda N)$ rather than the old result $\lambda S(E,V,N) = S(\lambda E, V, \lambda N)$]

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

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

(use $N = N_1 + N_2$)

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

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 <u>different</u> 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)

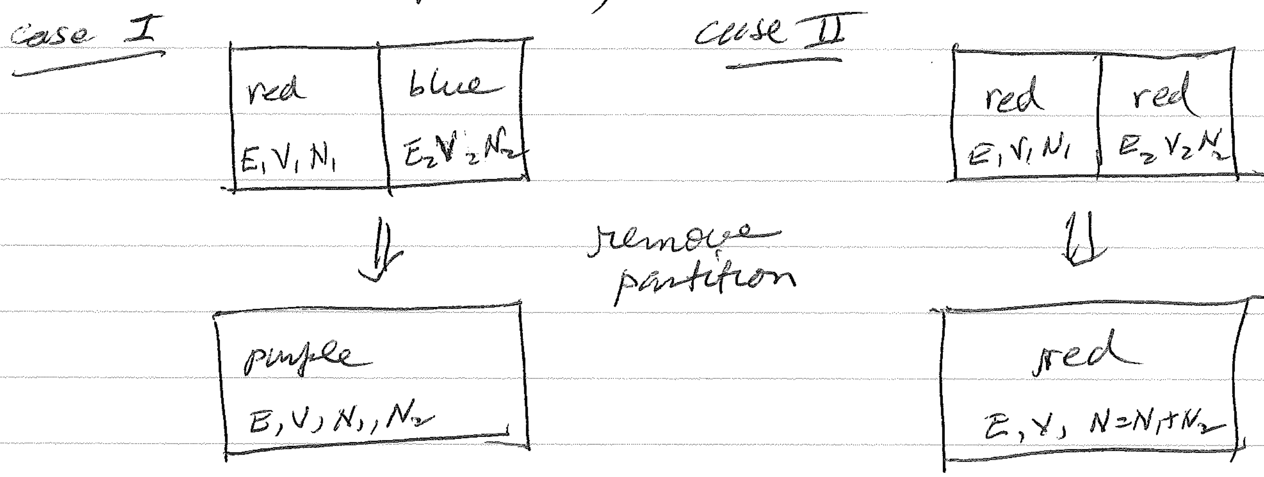
But if both gases are the same (ie we have only mentally divided them up into one group of N_1 and another of N_2) then it is <u>NOT</u> true that

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

This will not be true because the particles are <u>indistinguishable</u>. 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 $S(E,V,N) = 2S(\frac{E}{2}, \frac{V}{2}, \frac{N}{2})$!

A more general way to think about entropy of mixing and the indistinguishability of particles

- Initially gases on two sides of box at at same T and p
- when remove the partition, mixture will remain at the same T and p



$$\Delta S^{I} = S_f^{I} - S_i^{I} > 0 \quad \text{entropy of mixing} \qquad \Delta S^{II} = S_f^{II} - S_i^{II} = 0$$

If the red gas and the blue gas are exactly the same except for different colors, then we expect $S_i^{I} = S_i^{II}$. Then since $\Delta S^{II} = 0$ so $S_f^{II} = S_i^{II} = S_i^{I}$ we conclude

$$\Delta S^{I} = S_f^{I} - S_f^{II}$$

Now lets compute S_f^{I} and S_f^{II}

case I -

Consider the total number of states available to a system composed of the mixture of two gases with N_1 and N_2 particles respectively, both in vol V.

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

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

total # states available to the combined system

states available to particles in gas 1

states available to particles in gas 2

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

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

and then

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

$$\text{where } \left.\frac{\partial S_1}{\partial E_1}\right|_{E_1=\bar{E}_1} = \left.\frac{\partial S}{\partial E_2}\right|_{E_2=E-\bar{E}_1}$$

So $S_f^{I} = S_1(\bar{E}_1,V,N_1) + S_2(E-\bar{E}_1,V,N_2)$

Case II

Now suppose the two gases are the <u>same</u> type, ie red and red, so that the particles of gas 1 <u>cannot be distinguished</u> from the particles of gas 2, then

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

total # states available to the combined system

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

because of the indistinguishability of the two gases

ie $N_1!\,\Omega_1(E_1, V, N_1)$ is the number of <u>distinguishable</u> 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 <u>if</u> all particles are <u>distinguishable</u>

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

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

$$S_T(E, V, N_1, N_2) = S_1(\bar{E}_1, V, N_1) + S_2(E - \bar{E}_1, V, N_2) - k_B \ln\left(\frac{N!}{N_1! N_2!}\right)$$

So $S_f^{II} = S_1(\bar{E}_1, V, N_1) + S_2(E - \bar{E}_1, V, N_2) - k_B \ln\left(\frac{N!}{N_1! N_2!}\right)$

So entropy of mixing is

$$\Delta S^{I} = S_f^{I} - S_f^{II} = k_B \ln\left(\frac{N!}{N_1! N_2!}\right) \qquad N = N_1 + N_2$$

Using Stirlings formula $\ln N! \simeq N \ln N - N$
we get

$$\Delta S^{I} = k_B \left\{ N \ln N - N - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2 \right\}$$

$$= k_B \left\{ (N_1 + N_2) \ln N - N_1 \ln N_1 - N_2 \ln N_2 \right\}$$

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

This is the same result we got when we used the explicit formula for the entropy of the ideal gas