Entropy of mixing & Gibb's paradox:

Recall the previous expression for entropy:

$$S = Nk_B \ln\left[V\left(\frac{4\pi e m E}{3N}\right)^{3/2}\right] \qquad (1)$$

Above expression has a problem: S is not extensive!

Scale $(E, V, N) \longrightarrow (\lambda E, \lambda \overset{V}{\cancel{E}}, \lambda N)$, we see that

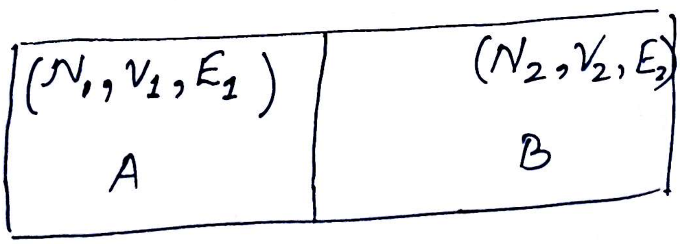
$$S \longrightarrow \lambda S + \underbrace{\lambda N k_B \ln \lambda}$$

Extra term makes S non-extensive.

"The extra term results due to the V^N contribution from accessible configurations to the total entropy."

In what follows, we shall show a deep connection between this extra term & entropy of mixing.

A mixing experiment:



Two compartments A & B contain different gases at same temperature (T).

The initial entropy is :

$$S_i^{\circ} = S_1 + S_2 = N_1 k_B \ln\left[V_1 \left(\frac{4\pi e m_1 E_1}{3N_1}\right)^{3/2}\right] + N_2 k_B \ln\left[V_2 \left(\frac{4\pi e m_2 E_2}{3N_2}\right)^{3/2}\right]$$

Since the temperature of the gas does not change after mixing, we write:

$$(3/2) k_B T = E_1/N_1 = E_2/N_2 = (E_1+E_2)/(N_1+N_2)$$

The final entropy is:

$$S_f = N_1 k_B \ln\left[V \left(\frac{4\pi e m_1 E_1}{3N_1}\right)^{3/2}\right] + N_2 k_B \ln\left[V \left(\frac{4\pi e m_2 E_2}{3N_2}\right)^{3/2}\right]$$

∴ The entropy of mixing is

$$\Delta S_{mix} = S_f - S_i^{\circ} = -N_1 k_B \ln(V_1/V) - N_2 k_B \ln(V_2/V)$$

$$= -N k_B \left[\frac{N_1}{N}\ln\left(\frac{V_1}{V}\right) + \frac{N_2}{N}\ln\left(\frac{V_2}{V}\right)\right] \quad \text{--- (2)}$$

Equation (2) can be generalized to include mixing of many components. That is,

$$\Delta S_{mix} = -N k_B \left[\sum_{\alpha} \frac{N_\alpha}{N}\ln\left(\frac{V_\alpha}{V}\right)\right]$$

The Gibbs's paradox is related to the observation made when two identical gases with same densities mix with each other. Clearly when such a mixing takes place then no entropy of mixing should be expected as removal of a partition does not produce any change to the state of the composite system. On the other hand, eq^n 2 predicts an entropy of mixing even when two identical gases at same densities mix with each other. We resolve this paradox as below.

"The problem is rooted in over counting the accessible phase space 'Ω' for the identical particles." the correct number of micro-states or accessible phase space volume for N-indistinguishable particles is.

$$\Omega(E,V,N) = \frac{V^N}{N!}\,\frac{2\pi^{3N/2}}{(3N/2-1)!}\,(2mE)^{(3N-1)/2}\,\Delta_R$$

This gives the entropy

$$S = k_B \ln \Omega = N k_B \ln\left[\frac{eV}{N}\left(\frac{4\pi e m E}{3N}\right)^{3/2}\right]$$

As you can see, this expression is properly extensive.
That is as $(E, V, N) \longrightarrow (\lambda E, \lambda V, \lambda N)$

$$S \longrightarrow \lambda S$$

Lets calculate the entropy of mixing of two distinct gases

$$\Delta S_{mix} = S_f - S_i$$

$$= N_1 k_B \ln\left(\frac{eV}{N_1}\alpha_1\right) + N_2 k_B \ln\left(\frac{eV}{N_2}.\alpha_2\right)$$

$$- \left(N_1 k_B \ln\left(\frac{eV_1}{N_1}\alpha_1\right) + N_2 k_B \ln\left(\frac{eV_2}{N_2}\alpha_2\right)\right)$$

where $\alpha_j = \left(\dfrac{4\pi e m_j E_j}{3N_j}\right)^{3/2}$

$$\therefore \Delta S_{mix} = -N_1 k_B \ln\left(\frac{V_1}{V}\right) - N_2 k_B \ln\left(\frac{V_2}{V}\right)$$

$$= -Nk_B\left[\frac{N_1}{N}\ln\left(\frac{V_1}{V}\right) + \frac{N_2}{N}\ln\left(\frac{V_2}{V}\right)\right]$$

which is the same expression as derived before without the correction in S.

If we now look at the mixing problem of two identical gases initially at the same densities : $\frac{N_1}{V_1} = \frac{N_2}{V_2}$

$= \frac{N}{V}$

then,
$$\Delta S_{mix} = S_f - S_i$$
$$= N k_B \ln\left[\frac{eV}{N}\left(\frac{4\pi e m E}{3N}\right)^{3/2}\right] - \sum_{\alpha=1,2} N_\alpha k_B \ln\left[\frac{eV_\alpha}{N_\alpha}\left(\frac{4\pi e m E_\alpha}{3N_\alpha}\right)^{3/2}\right]$$

$$= 0$$

Hence Gibb's paradox stands resolved!

"The mixing of identical gases at same densities and temparature is zero".