Gibbs' Paradox

Gibbs paradox appears when we mix two similar ideal gases.

(A) *Mixing of two different ideal gases at constant temperature*: The mixing of two different gases is an irreversible process. If we consider mixing of two different gases (N_1,V_1,T) and (N_2,V_2,T) with V= V_1+ V_2 and N= N_1+ N_2 then the change in entropy of (**) is

$$\Delta S = S - (S_1 + S_2) = N_1 k \ln\left(\frac{V}{V_1}\right) + N_2 k \ln\left(\frac{V}{V_2}\right) > 0\,,$$

This gives the entropy of mixing for two different ideal gases and is in agreement with experiments. For N_1= N_2=N, V_1= V_2=V/2 , we get $\Delta S = 2Nk\ln 2$.

(B) *Mixing of the same two ideal gases at constant temperature*: If the two gases are the same, the process is **reversal** one. The final entropy ought to be the same with, or without mixing, then the change in entropy is

$$\Delta S = S - (S_1 + S_2) = 0\,.$$

This result is in agreement with the thermodynamics of revisable processes and also with experiments, but contradict Eq. (**). The derivation of Eq. (**) does not depend on the identity of the molecules and would give the same increase in entropy as two different gases.

Comments:

1- In the case (A), mixing leads to diffusion of the molecules through the whole volume V (twice the initial volumes). There is a random mixing of the different molecules and so an increase in the disorder. This irreversible process and the increase of entropy make sense. The mixing is a process in which the positions of molecules one gas are interchanged with those of the other gas. Each such exchange creates a new states, i.e. increasing the number of microstates or equivalently the entropy increases.

2- In case (B), any such interchange is always an interchange between two identical molecules. Therefore, no new state is created. In this case, the application of Eq. (**) overestimates the number of accessible states because classically we have taken all the molecules, even of the same gas, as distinguishable. To solve this paradox, we have to change Z by $z^N/N!$ The final results read

$$\ln Z = N\ln z - (N\ln N - N),$$

$$S = Nk\left[\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma_o{}^*\right] \quad , \qquad (+)$$

where $\sigma_o{}^* = S_o + 1 = \frac{3}{2}\ln\left(\frac{2\pi mk}{h^2}\right) + \frac{5}{2}$.

Eq. (+) has the properties of the entropy, and gives the correct answer for both cases, but it is not accurate at very low temperature.

Example: Using the corrected entropy formula (Sackur-Tetrode equation)

$$S = kN\ln\frac{V}{N} + +\frac{3}{2}kN\left[\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{5}{2}\right],$$

work out the entropy of mixing for the case of different gases and for identical gases, thus showing explicitly that there is no Gibbs paradox.

Answer:

(A) Mixing of two different ideal gases at the same temperature, the entropies of the gases before mixing are:

$$S_i = kN_i\ln\frac{V_i}{N_i} + \frac{3}{2}kN_i\left[\ln\left(\frac{2\pi m_i kT}{h^2}\right) + \frac{5}{2}\right], \quad i = 1,2\,,$$

Mixing of the gases in the volume $V=V_1+V_2$ implies the total entropy after mixing is

$$S_{total} = \sum_{i=1}^{2}\{kN_i\ln\frac{V}{N_i} + \frac{3}{2}kN_i\left[\ln\left(\frac{2\pi m_i kT}{h^2}\right) + \frac{5}{2}\right]\}$$

The entropy of mixing for the case of two different gases is:

$$\Delta S = S_{total} - (S_1 + S_2) = kN_1\ln\frac{V}{V_1} + kN_2\ln\frac{V}{V_2}$$

i.e. $\Delta S > 0$ for the mixing of two different gases.

(B) Mixing of two identical gases: $m_1 = m_2 = m$. Assume the densities are the same, i.e. $\frac{N}{V} = \frac{N_1}{V_1} = \frac{N_2}{V_2}$, then

$$S_{total} = kN\ln\frac{V}{N} + \frac{3}{2}kN\left[\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{5}{2}\right]$$

has the properties of the entropy, and gives the correct answer for both cases, but it is not accurate at very low temperature.

The entropy of mixing is

$$\Delta S = S_{total} - (S_1 + S_2) = Nk\ln(\frac{V}{N}) - N_1k\ln(\frac{V_1}{N_1}) - N_2k\ln(\frac{V_2}{N_2})$$

$$= k(N - N_1 - N_2)\ln\frac{V}{N} = 0$$

$\Delta S = 0$ for the mixing of two identical gases with the same particle density, i.e. no Gibbs paradox.