

## The entropy of mixing and the Gibbs paradox

The entropy of an ideal gas given by the expression is not an extensive property of the system. That is if we increase the size of the system by a factor  $\alpha$ , keeping the intensive variables unchanged, then the entropy of the system which should also increase by a factor  $\alpha$ , does not do so; the presence of the  $\ln V$  term in the expression affect the result adversely. It means that the entropy of the system is different from the sum of the entropies of its parts, which is quite unphysical. A more common way of looking at this problem is to consider so - called Gibbs paradox.

Gibbs visualized the mixing of two ideal gases 1 and 2, both being initially at the same temperature  $T$ , then the temperature of the mixture will be same. Before mixing the respective entropies of the two gases were.

$$S_i = N_i k \ln V_i + \frac{3}{2} N_i k \left\{ 1 + \ln \left( \frac{2\pi m_i k T}{h^2} \right) \right\}; \quad i = 1, 2, \dots \rightarrow (1)$$

After mixing has taken place, the total entropy will be

$$S_T = \sum_{i=1}^2 [N_i k \ln V + \frac{3}{2} N_i k \left\{ 1 + \ln \left( \frac{2\pi m_i k T}{h^2} \right) \right\}] \rightarrow (2)$$

Where  $V = V_1 + V_2$ , thus the net increase in the value of  $S$ , which may be called the entropy of mixing, is given by

$$\Delta S = S_T - \sum_{i=1}^2 S_i = k \left[ N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2} \right] \rightarrow (3)$$

The quantity  $\Delta S$  is indeed positive as it must be for an irreversible process like mixing. Now, in the special case when initial particle densities of the two gases are also the same.

$$(\Delta S)^* = k \left[ N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2} \right] \rightarrow (4)$$

Which is again positive.

However a paradoxical situation arises if we consider the mixing of two samples of two gases. Once again, the entropies of the individual gases given by (1), now  $m_1 = m_2 = m$ . Then entropy of mixing will be

$$S_T = NK \ln V + \frac{3}{2} Nk \left\{ 1 + \ln \left( \frac{2\pi mkT}{h^2} \right) \right\} \quad (5)$$

When  $N = N_1 + N_2$ ; this expression is numerically same as (2) with  $m_i = m$ . Therefore the entropy of mixing will be given by (3).

$$\text{if } N_1/V_1 = N_2/V_2 = (N_1 + N_2) / (V_1 + V_2) \text{ By (4).}$$

The last conclusion is unacceptable because the mixing of two samples of same gases, with a common initial temperature  $T$  and a common initial particle density  $n$  is clearly a reversible process, for we can simply reinsert a partition wall into the system and obtain a situation that is no way different from one we had before mixing. When two dissimilar gases, even with a common initial temperature  $T$ , and a common initial particle density  $n$ , mixed together the process was irreversible, for by reinserting the partitioning wall one would obtain two samples of the mixture and not the two gases that were originally present; to that case.

$$(\Delta S)^* = 0$$

The foregoing result would also be consistent with the requirement that the entropy of a given system is equal to the sum of the entropies of its parts. For the entropy of mixing of two samples of the same gas, with a common  $T$  and a common  $n$ , the result can be written as

$$(\Delta S)^* = S_T - (S_1 + S_2) \approx k [ \ln (N_1 + N_2)! ] - \ln (N_1!) - \ln (N_2!) \quad (6)$$

The modified expression for entropy of classical ideal gas would be

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

$$= NK \ln \left( \frac{V}{N} \right) + \frac{3}{2} NK \left\{ \frac{5}{3} + \ln \left( \frac{2\pi m k T}{h^2} \right) \right\}$$

If we mix two samples of the same gas at common initial temperature T, the entropy of mixing will be

$$(\Delta S)_{1 \equiv 2} = k \left[ (N_1 + N_2) \ln \frac{(V_1 + V_2)}{(N_1 + N_2)} - N_1 \ln \left( \frac{V_1}{N_1} \right) - N_2 \ln \left( \frac{V_2}{N_2} \right) \right]$$

If the initial densities of the samples were also equal, the result would be

$$(\Delta S)_{1 \equiv 2}^* = 0$$

The expression for the energy E of the gas, written as the function of N, V, and S is also modified.

$$E(N, V, S) = \frac{3h^2 N^{5/3}}{4\pi m V^{2/2}} \exp \left( \frac{2S}{3NK} - \frac{5}{3} \right)$$

Chemical potential of the gases is given by

$$\mu = \left( \frac{\partial E}{\partial N} \right)_{V, S} = E \left[ \frac{5}{3N} - \frac{3S}{3N^2 K} \right] \quad (7)$$

Also  $\mu$  can be written as

$$\mu = \frac{1}{N} [ E + PV - TS ] \equiv \frac{G}{N} \quad (8)$$

Where G is the Gibbs free energy of the system, in terms of variables N, V, T ;  $\mu$  can be written as

$$\mu(N, V, T) = KT \ln \left\{ \frac{N}{V} \left( \frac{h^2}{2\pi m KT} \right)^{3/2} \right\} \quad (9)$$

Another quantity of importance is the Helmholtz free energy

$$A = E - TS = G - PV = NKT \left[ \ln \left\{ \frac{N}{V} \left( \frac{h^2}{2\pi m KT} \right)^{3/2} \right\} - 1 \right]$$