The Entropy of Mixing and Gibss Paradox

One thing we readily observe from the following expression

$$S = k \ln \Gamma = Nk \ln\left\{\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\} + \frac{3}{2}Nk$$

is that, contrary to what is logically desired, the entropy of an ideal gas, as given by this expression, is not an extensive property of the system!

That is, if we increase the size of the system by a factor λ, keeping the intensive variables unchanged, then the entropy of the system, which should also increase by the same factor λ, does not do so; the presence of the In V term in the expression affects the result adversely.

$$S = k \ln \Gamma = Nk \ln\left\{\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\} + \frac{3}{2}Nk$$

$$(N \quad V \quad E) \Rightarrow (\lambda N \quad \lambda V \quad \lambda E)$$

$$S(\lambda N, \lambda V, \lambda E) = \lambda Nk \ln\left\{\frac{\lambda V}{h^3}\left(\frac{4\pi m \lambda E}{3\lambda N}\right)^{\frac{3}{2}}\right\} + \frac{3}{2}\lambda Nk$$

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

This in a way means that the entropy of the system is different from the sum of the entropies of its parts, which is absurd.

A more common way of looking at this problem is to consider the so-called Gibbs paradox.

Gibbs visualized the mixing of two ideal gases 1 and 2, both being initially at the same temperature T.

Clearly, the temperature of the mixture would also be the same.

Now, before the mixing took place, the respective entropies of the two gases were:

$$S_i = N_i k \ln\left\{\frac{V_i}{h^3}\left(\frac{4\pi m_i E}{3N_i}\right)^{\frac{3}{2}}\right\} + \frac{3}{2}N_i k$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V} = \frac{2}{3}\frac{E}{Nk} \quad \Rightarrow \quad E = \frac{3}{2}Nk$$

$$S_i = N_i k \ln\left\{\frac{V_i}{h^3}\left(\frac{4\pi m_i \cancel{\frac{3}{2}} N_i kT}{\cancel{3N_i}}\right)^{\frac{3}{2}}\right\} + \frac{3}{2}N_i k$$

$$S_i = N_i k \ln\left\{\frac{V_i}{h^3}\left(\frac{2\pi m_i kT}{1}\right)^{\frac{3}{2}}\right\} + \frac{3}{2}N_i k$$

$$S_i = N_i k \ln\left\{\frac{V_i}{1}\left(\frac{2\pi m_i kT}{h^2}\right)^{\frac{3}{2}}\right\} + \frac{3}{2}N_i k$$

$$S_i = N_i k \ln\left\{\frac{V_i}{1}\right\} + N_i k \ln\left\{\left(\frac{2\pi m_i kT}{h^2}\right)^{\frac{3}{2}}\right\} + \frac{3}{2}N_i k$$

$$S_i = \frac{3}{2}N_i k \ln\left(\frac{2\pi m_i kT}{h^2}\right) + \frac{3}{2}N_i k + N_i k \ln V_i$$

$$S_i = \frac{3}{2}N_i k\left\{1 + \ln\left(\frac{2\pi m_i kT}{h^2}\right)\right\} + N_i k \ln V_i$$

After the mixing has taken place, the total entropy would be

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

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

$$\Delta S = S_T - \sum_{i=1}^{2} S_i = \sum_{i=1}^{2}\left(\frac{3}{2}N_i k\left\{1 + \ln\left(\frac{2\pi m_i kT}{h^2}\right)\right\} + N_i k \ln V\right) -$$

$$- \sum_{i=1}^{2}\left(\frac{3}{2}N_i k\left\{1 + \ln\left(\frac{2\pi m_i kT}{h^2}\right)\right\} + N_i k \ln V_i\right) =$$

$$= \sum_{i=1}^{2}\left(\frac{3}{2}N_i k\left\{1 + \ln\left(\frac{2\pi m_i kT}{h^2}\right)\right\}\right) + \sum_{i=1}^{2} N_i k \ln V -$$

$$- \sum_{i=1}^{2}\left(\frac{3}{2}N_i k\left\{1 + \ln\left(\frac{2\pi m_i kT}{h^2}\right)\right\}\right) - \sum_{i=1}^{2} N_i k \ln V_i =$$

$$\Delta S = S_T - \sum_{i=1}^{2} S_i = \sum_{i=1}^{2} N_i k \ln V - \sum_{i=1}^{2} N_i k \ln V_i =$$

$$= \sum_{i=1}^{2}\left(N_i k \ln V - N_i k \ln V_i\right) =$$

$$= \sum_{i=1}^{2} N_i k \ln \frac{V}{V_i} =$$

$$= N_1 k \ln \frac{V}{V_1} + N_2 k \ln \frac{V}{V_2}$$

$$= N_1 k \ln \frac{V_1 + V_2}{V_1} + N_2 k \ln \frac{V_1 + V_2}{V_2}$$

$$\Delta S = k\left(N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2}\right)$$

The quantity ΔS is indeed positive, as it must be for an irreversible process like mixing.

$V_1 + V_2 > V_1$
$V_1 + V_2 > V_2$
$N_1 \,\&\, N_2 > 0$

$$\Rightarrow \quad \left(N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2}\right) > 0$$

$k > 0$

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

Now, in the special case when the initial particle densities of the two gases (and, hence, the particle density of the mixture) are also the same

$$n_1 = \frac{N_1}{V_1} = n_2 = \frac{N_2}{V_2} = n = \frac{N}{V} = \frac{N_1 + N_2}{V_1 + V_2}$$

$$(\Delta S)^* = k\left(N_1 \ln \frac{\frac{N_1 + N_2}{n}}{\frac{N_1}{n_1}} + N_2 \ln \frac{\frac{N_1 + N_2}{n}}{\frac{N_2}{n_2}} \right)$$

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

which is again positive.

So far, it seems all right. However, a paradoxical situation arises if we consider the mixing of two samples of the same gas. Once again, the entropies of the individual samples will be given by (1); of course, now $m_1 = m_2 = m$, say. And the entropy after mixing will be given by

$1 \equiv 2$ ⟹

$$S_i = \frac{3}{2} N_i k \left\{ 1 + \ln\left(\frac{2\pi m k T}{h^2} \right) \right\} + N_i k \ln V_i$$

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

$$(\Delta S)^*_{1=2} = k\left(N_1 \ln \frac{N_1 + N_2}{N_1} + N_2 \ln \frac{N_1 + N_2}{N_2} \right) = (\Delta S)^*$$

The last conclusion ($\Delta S^* > 0$), however, is unacceptable because the mixing of two samples of the same gas, with a common initial temperature T and a common initial particle density n, is clearly a reversible process, for we can simply reinsert the partitioning wall into the system and obtain a situation which is in no way different from the one we had before mixing.

Of course, we tacitly imply that in dealing with (a system of) identical particles we cannot track them down individually; all we can reckon with is their numbers. When two dissimilar gases, even with a common initial temperature and a common initial particle density, 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, expression (4) would indeed apply. However, in the present case (two similar gases), the corresponding result should be

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

The foregoing result would also be consistent with the requirement that the entropy of a given system be equal to the sum of the entropies of its parts.

$$(\Delta S)^*_{1=2} = 0 \Longrightarrow S_T - \sum_{i=1}^{2} S_i = 0 \Longrightarrow S_T = S_1 + S_2 \ \text{☺}$$

Of course, we had already noticed that this is not ensured by expression (1.4.21). Thus, once again we are led to believe that there is something basically wrong with that expression.

To see how the above paradoxical situation can be avoided, we recall that, for the entropy of mixing of two samples of the same gas, with a common T and a common n, we were led to result (4), which can also be written as

$$(\Delta S)^*_{1=2} = k\left(N_1 \ln \frac{N_1 + N_2}{N_1} + N_2 \ln \frac{N_1 + N_2}{N_2} \right) =$$

$$= k\left(N_1 \ln(N_1 + N_2) - N_1 \ln N_1 + N_2 \ln(N_1 + N_2) - N_2 \ln N_2 \right) =$$

$$= k\left((N_1 + N_2)\ln(N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2 \right) =$$

$$= k\left((N_1 + N_2)\ln(N_1 + N_2) - (N_1 + N_2) + (N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2 \right) =$$

$$= k\left(\ln(N_1 + N_2)! - \left[N_1 \ln N_1 - N_1 + N_2 \ln N_2 - N_2 \right] \right) =$$

$$= k\left(\ln(N_1 + N_2)! - \ln N_1 ! - \ln N_2 ! \right)$$

$$(\Delta S)^{*}_{1=2} = k\left(\ln(N_1+N_2)!-\ln N_1!-\ln N_2!\right)$$

$$S_{Old} = k\ln\Gamma = Nk\ln\left\{\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\}+\frac{3}{2}Nk$$

$$S_{New} = k\ln\Gamma_{New} = Nk\ln\left\{\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\}+\frac{3}{2}Nk-k\ln N!$$

$$S_{New} = k\ln\Gamma_{New} = Nk\ln\left\{\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\}+\frac{3}{2}Nk-Nk\ln N+kN$$

$$S_{New} = k\ln\Gamma_{New} = Nk\ln\left\{\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\}+\frac{3}{2}Nk+kN$$

$$S_{New} = k\ln\Gamma_{New} = Nk\ln\left\{\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\}+\frac{5}{2}Nk$$

$$S_{New} = k\ln\Gamma_{New} = Nk\ln\left\{\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\}+\frac{5}{2}Nk$$

$$S_{New} = k\ln\Gamma_{New} = k\ln\Gamma_{old} - nk\ln N!$$

$$= k\ln\frac{\Gamma_{old}}{N!}$$

$$\Gamma_{New} = \frac{\Gamma_{old}}{N!}$$

درستی روابط زیر را با استفاده از تصحیح گیبس، S_{New}، تحقیق کنید:

$$\Delta S_{New} > 0$$

$$(\Delta S_{New})^{*} > 0$$

$$(\Delta S_{New})^{*}_{1=2} = 0$$ ☺

Sackur-Tetrode equation:

$$S = k\ln\Gamma = Nk\ln\left\{\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\}+\frac{5}{2}Nk$$

$$S-\frac{5}{2}Nk = Nk\ln\left\{\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\}$$

$$\frac{S-\frac{5}{2}Nk}{Nk} = \ln\left\{\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\}$$

$$\frac{S}{Nk}-\frac{5}{2} = \ln\left\{\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\}$$

$$\exp\left\{\frac{S}{Nk}-\frac{5}{2}\right\} = \frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}$$

$$\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}} = \frac{Nh^3}{V}\exp\left\{\frac{S}{Nk}-\frac{5}{2}\right\}$$

$$\frac{4\pi mE}{3N} = \left(\frac{Nh^3}{V}\right)^{2/3}\exp\left\{\frac{2S}{3Nk}-\frac{2}{3}\frac{5}{2}\right\}$$

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

$$E = \frac{3N^{5/3}h^2}{4\pi mV}\exp\left\{\frac{2S}{3Nk}-\frac{5}{3}\right\}$$

کدامیک از کمیتهای ترمودینامیکی پس از تصحیح گیبس تغییر می کنند و کدامیک بدون تغییر باقی می مانند؟

روابط یا کمیتهـای بدون تغییر؟

$$dE = TdS - PdV + \mu dN$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} = \frac{2}{3Nk}E \Rightarrow E = \frac{3}{2}NkT$$

$$P = -\left(\frac{\partial E}{\partial V}\right)_{S,N} = \frac{2}{3}\frac{E}{V} \Rightarrow PV = \frac{2}{3}E = \frac{2}{3}\times\frac{3}{2}NkT \Rightarrow PV = NkT$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = \frac{3}{2}Nk$$

$$C_P = \frac{\partial(E+PV)}{\partial T} = \frac{5}{2}Nk$$

$$\gamma = \frac{C_P}{C_V} = \frac{5}{3}$$

$$\frac{E_f}{E_i} = \left(\frac{V_i}{V_f}\right)^{\frac{2}{3}} \Rightarrow E_f V_f^{\frac{2}{3}} = E_i V_i^{\frac{2}{3}} = EV^{\frac{2}{3}} = cte \Rightarrow$$

$$\frac{3}{2}NkTV^{\frac{2}{3}} = cte \Rightarrow TV^{\gamma-1} = cte$$

$$PV = NkT \Rightarrow PV^{\gamma} = cte$$

کمیتهای تغییر یافته؟

$$E = \frac{3N^{5/3}h^2}{4\pi mV}\exp\left\{\frac{2S}{3Nk} - \frac{5}{3}\right\}$$

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} = \frac{5}{3}\frac{E}{V} - \frac{1}{N^2}\frac{2S}{3k}E = E\left(\frac{5}{3N} - \frac{2}{3}\frac{S}{N^2k}\right) = \frac{3}{2}NkT\left(\frac{5}{3N} - \frac{2S}{3N^2k}\right) =$$

$$S = Nk\ln\left\{\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right\} \quad \frac{5}{2}Nk$$

$$= \frac{5}{2}kT - \frac{ST}{N} = \frac{5}{2}kT - kT\ln\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}} - \frac{5}{2}kT = kT\ln\frac{Nh^3}{V}\left(\frac{3N}{4\pi mE}\right)^{\frac{3}{2}} =$$

$$= kT\ln\frac{N}{V}\left(\frac{h^2}{2\pi mNkT}\right)^{\frac{3}{2}}$$

پس μ نافزونور است.

روش دوم محاسبه μ

$$E = TS - PV + \mu N$$

$$\mu = \frac{E - TS + PV}{N} = \frac{\frac{3}{2}NKT - TS + NKT}{N}$$

$$\mu = \frac{5}{2}KT - \frac{ST}{N}$$

ادامه مانند صفحه قبل

$$E = TS - PV \quad \mu N$$

$$\mu = \frac{E - TS \quad PV}{N} = \frac{G}{N}$$

$$G = \mu N$$

$$G = N\left\{kT\ln\frac{N}{V}\left(\frac{h^2}{2\pi mNkT}\right)^{\frac{3}{2}}\right\}$$

پس G فزونور است.

$$A = E - TS$$

$$G = E \quad PV - TS$$

$$G - PV = E - TS = A$$

$$A = G - PV =$$

$$A = G - NkT =$$

$$= NkT\ln\frac{N}{V}\left(\frac{h^2}{2\pi mNkT}\right)^{\frac{3}{2}} - NkT = NkT\left\{\ln\frac{N}{V}\left(\frac{h^2}{2\pi mNkT}\right)^{\frac{3}{2}} - 1\right\}$$