PHYS 3014: Statistical Mechanics

Lecture Notes
Part 2

Entropy of Mixing: Gibbs Paradox

Programme: B. Sc. Physics
Semester: VI

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Entropy of Mixing : Gibbs Paradox

The entropy of an ideal gas is an extensive quantity. If we increase the size of the system by a factor α, keeping the intensive variable unchanged, then the entropy of the system must increase by the same factor α.

Entropy of the system

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

change $V \longrightarrow \alpha V$, $N \longrightarrow \alpha N$ and $E \longrightarrow \alpha E$

Keeping $\frac{E}{N}$ Constant

Entropy of the new system

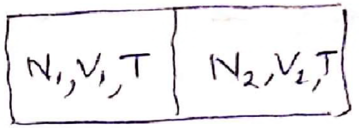
$$S' = \alpha N K \ln\left\{ \frac{\alpha V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right\} + \frac{3}{2} \alpha N K$$

$$= \alpha S + \alpha N K \ln \alpha$$

The new expression for the entropy fails to satisfy the additive property of the entropy. The entropy of the system is different from the sum of the entropies of its parts which is absurd. This is contradictory and is called as Gibbs paradox.

Consider two ideal gases 1 and 2 both are at the same temperature T.

The entropies of two gases are



$$S_1 = N_1 k \ln V_1 + \frac{3}{2} N_1 k \left[1 + \ln\left(\frac{2\pi m_1 k T}{h^2}\right)\right]$$

$$S_2 = N_2 k \ln V_2 + \frac{3}{2} N_2 k \left[1 + \ln\left(\frac{2\pi m_2 k T}{h^2}\right)\right] \quad \text{---} ①$$

Gibbs considered the mixing of two gases by vanishing the partition between two so that now gases occupy a volume $V_1 + V_2$ keeping temperature same.

Total entropy

$$S_T = N_1 k \ln(V_1 + V_2) + \frac{3}{2} N_1 k \left[1 + \ln\left(\frac{2\pi m_1 k T}{h^2}\right)\right]$$
$$+ N_2 k \ln(V_1 + V_2) + \frac{3}{2} N_2 k \left[1 + \ln\left(\frac{2\pi m_2 k T}{h^2}\right)\right] \quad \text{--} ②$$

The net increase in the value of S which is called as the entropy of mixing is given by

$$\Delta S = S_T - S_1 - S_2$$

$$= K\left[N_1 \ln\left(\frac{V_1+V_2}{V_1}\right) + N_2 \ln\left(\frac{V_1+V_2}{V_2}\right)\right] \quad \text{--} ③$$

$\because$ V_1+V_2 is always greater than V_1 and V_2, so ΔS is always positive. It is usual for any irreversible process like mixing.

If the initial particle densities of two gases is same i.e

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} \Rightarrow \frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1+N_2}{V_1+V_2}$$

the particle density of mixture is also same.

So equation ③ becomes

$$(\Delta S)^* = k\left[N_1 \ln\left(\frac{N_1+N_2}{N_1}\right) + N_2 \ln\left(\frac{N_1+N_2}{N_2}\right)\right] \quad \text{--} ④$$

It is again positive.

Now a paradoxial situation arises when there is mixing of two samples of same gas.

$$m_1 = m_2 = m, \quad N = N_1 + N_2, \quad V = V_1 + V_2$$

Such mixing is reversible.

Entropy after mixing

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

change in entropy

$$\Delta S = S_T - S_1 - S_2$$

$$= (N_1+N_2)k \ln(V_1+V_2) - N_1 k \ln V_1 - N_2 \ln V_2$$

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

If particle density is same then

$$(\Delta S)^* = K\left[N_1 \ln\left(\frac{N_1+N_2}{N_1}\right) + N_2 \ln\left(\frac{N_1+N_2}{N_2}\right)\right] \quad \text{--} ⑥$$

So change in entropy is positive for the mixing of two samples of same gas at same temperature. Such mixing is reversible so change must be zero. Therefore, we have a paradoxial situation.

The entropy of mixing with a common temperature T and common particle density n

$$(\Delta S)^* = S_T - S_1 - S_2$$

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

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

$$\therefore \; (\Delta S)^* \simeq K\left[\ln \underline{|(N_1+N_2)} - \ln \underline{|N_1} - \ln \underline{|N_2}\right]$$

If original expression for S were diminished by $K \ln \underline{|N}$, then $(\Delta S)^*$ would ultimately come out to be zero. It means that statistical numbers Γ and Σ, must be reduced by a factor $\underline{|N}$.

Gibbs solved the paradox by considering gas molecules completely identical and indistinguishable i-e N molecules of the system cannot be distinguished by $\underline{|N}$ ways. So entropy of the system must be given by

$$S = K \ln\left(\frac{\Gamma}{\underline{|N}}\right)$$

$$= K \ln \Gamma - K \ln \underline{|N}$$

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

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

$$= NK \ln \left(\frac{V}{N} \right) + \frac{3}{2} NK \ln \left(\frac{4\pi m E}{3N h^2} \right) + \frac{5}{2} NK$$

$$\therefore \quad S(N,V,E) = NK \ln \left(\frac{V}{N} \right) + \frac{3}{2} NK \left[\frac{5}{3} + \ln \left(\frac{2\pi m K T}{h^2} \right) \right]$$

$$E = \frac{3}{2} NKT$$

This relation is known as Sackur-Tetrode equation.

Now mix two samples of same gas at common initial temperature T, the entropy of mixing

$$(\Delta S) = K \left[(N_1 + N_2) \ln \left(\frac{V_1 + V_2}{N_1 + N_2} \right) - N_1 \ln \left(\frac{V_1}{N_1} \right) - N_2 \ln \left(\frac{V_2}{N_2} \right) \right]$$

when particle densities are same,

$$(\Delta S)^* = 0$$ as it should be.

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

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

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

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

G is Gibbs free energy of the system.

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

Helmholtz free energy

$$F = E - TS = G - PV$$

$$= NKT\left[\ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right] - 1\right]$$

F is an extensive property of the system and μ is intensive property of the system.

References:

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Thank You

For any questions/doubts/suggestions and submission of assignments

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