~~Canonical En~~

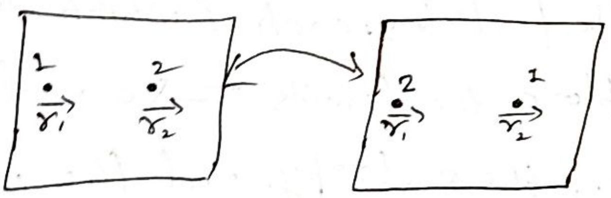
Gibbs Paradox

Using the concept of microcanonical ensemble, we obtain for an ideal gas (classical)

$$\Sigma(E) = \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)} V^N (2mE)^{\frac{3N}{2}} \quad \text{--- (1)}$$

$\Sigma(E) \rightarrow$ denotes volume in P-space enclosed by a surface of energy E.

Relation (1) leads to several paradoxes if we compute the mixing entropy of identical gases.



Gibbs resolved the paradox in an empirical way. He argued that $\Sigma(E)$ has been overcounted because permutations of identical particles do not count as an independent state. ~~He taken~~ Gibbs assumed $\Sigma(E)$, the number of states of the gas with energy less than E, N! times smaller than ~~the original~~ calculated by the expression (1)

$$\text{Thus} \quad \Sigma(E) = \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)} \frac{V^N}{N!} (2mE)^{\frac{3N}{2}} \quad \text{--- (2)}$$

Now the entropy 'S' is given by

$$S = k \ln \Sigma(E) \quad \text{--- (3)}$$

Taking $\ln N! = N\ln N - N$, we obtain from (2) and (3)

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

The modification done by Gibbs does not affect equation of state and other thermodynamic functions of a system.

H.W. (1) Using the microcanonical ensemble, compute Helmholtz ~~harmonic~~ free energy $F(T,N)$ as a function of temperature for a system of N identical but distinguishable particles; each of which has two energy levels. Explore the limits $T \to 0$ and $T \to \infty$ of the energy, the entropy and the occupation numbers.

(2) The internal energy $\bar{E}$ of a single component thermodynamic system expressed as a function of entropy S, and volume V is of the form

$$E(S,V) = aS^{4/3}V^{\alpha},$$ where a and α are constants.

Obtain the following:

(i) value of α. (ii) temperature of the system

(iii) pressure of the system