

**Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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**Lecture – 63
Thermodynamic Probability for Distinguishable Particles**

So we have talked about the Gibbs paradox so Gibbs paradox was about the fact that entropy which is an extensive property was not shown to be extensive where you have shown that S prime instead of being $2S$ it had an extra term $2 \ln 2$ and that is called Gibbs paradox and the source of Gibbs paradox was the over counting of the microstates. And if you go to further basics this over counting of microstates was due to the wrong definition of thermodynamic probability. So, in the thermodynamic probability we assumed that particles are distinguishable.

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$$W_D = \frac{N!}{n_1! n_2! n_3! \dots}; N \equiv \text{Total no. of particles}$$

$$= \frac{N!}{\prod n_i!}$$

$$\begin{array}{l} \epsilon_1 - \square\square\square \\ \epsilon_2 - \square \\ \epsilon_3 - \end{array} \left. \vphantom{\begin{array}{l} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \end{array}} \right\} \text{Energy levels}$$

$$\epsilon_i \rightarrow g_i \text{ fold degenerate}$$

And we defined W that thermodynamic probability for distinguishable particles as

$$W_D = \frac{N!}{n_1! n_2! n_3! \dots}$$

N is total number of particles in the system total number of particles and so it was n factorial n_1 factorial n_2 factorial n_3 factorial and so on, well you know n_1, n_2, n_3 are the number of particles in energy state 1, 2 and 3 which nothing but N factorial divided by n_i factorial this is the product of all small n 's.

So, this is the thermodynamic probability we got for the distinguishable particles. Now before we find out the thermodynamic probability for the indistinguishable particles, let us find out W_D in terms of the energy levels. So, what I mean by energy levels versus energy states. So, if I have 2 energy states one is here one is there. So, this is energy state with energy ϵ_i this is my energy state with ϵ_j and so on.

So, this energy state ϵ_i is let us say it is one fold degenerate whereas as the energy state above let us say it is 3 fold degenerate it is like your S orbital's and P orbital's. So, this is the energy levels, these are the energy levels. So, energy states is can be further considered in terms of energy levels. So, let us consider a system where my i th energy state with energy ϵ_i for that particular energy state is g_i fold degenerate.

So, if my i th energy state is g_i fold degenerate then how I can write my W_D in terms of the energy levels.

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W_D in terms of energy levels.

$$S = -Nk \sum p_i \ln p_i$$

$$= -Nk (p_1 \ln p_1 + p_2 \ln p_2 + p_3 \ln p_3 + \dots)$$

For a case where energy state ϵ_i is 3-fold degenerate,
let's say the energy levels are: $\epsilon_{i_1} = \epsilon_{i_2} = \epsilon_{i_3} = \epsilon_i$

Therefore, total entropic contribution of these levels to the energy state \Rightarrow

So, my goal is to write W_D in terms of energy levels. So, to do that let us make use of the expression of entropy again. So, if you recall entropy we defined as S

$$S = -NK \sum \rho_i \ln \rho_i$$

. Now let us consider a special case where my energy state i is 3 fold degenerate.

So, for a case where energy state with energy ϵ_i is 3fold degenerate. So, in this case my entropy you can write as rho so it is 3 fold here so I can write so for this case for energy state ϵ_i 3 fold

degenerate let us say that energy levels are ϵ_{11} and that is going to be equal to ϵ_{12} that is going to be ϵ_{13} because it is a degenerate state.

So, therefore all 3 levels to have same energy. So, all the 3 energy levels 11 12 13 all do have the same energy of ϵ_1 . So, therefore total entropic contribution of these levels to energy state will be ρ_{11} .

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$$\rho_{l1} \ln \rho_{l1} + \rho_{l2} \ln \rho_{l2} + \rho_{l3} \ln \rho_{l3} = 3\rho_{l1} \ln \rho_{l1}$$

$$3\rho_{l1} = \rho_l$$

$$\rho_{l1} = \frac{\rho_l}{3} = \frac{\rho_l}{g_l}$$

Hence

$$S = -Nk \sum_l \rho_l \ln \frac{\rho_l}{g_l}$$

$$= -k \sum_l n_l \ln \frac{n_l}{N g_l}$$

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$$S = -k \sum_l n_l \ln \frac{n_l}{N g_l}$$

$$= -k \sum_l n_l \ln n_l + k \sum_l n_l \ln g_l + k \sum_l n_l \ln N$$

$$= k [N \ln N + \sum_l n_l \ln g_l - \sum_l n_l \ln n_l]$$

$$= k [N \ln N - N + N - \sum_l n_l \ln n_l + \sum_l n_l \ln g_l]$$

$$= k [\ln N! + \sum_l n_l \ln g_l - \sum_l n_l \ln n_l]$$

$$= k [\ln N! + \sum_l n_l \ln g_l - \ln \sum_l n_l!]$$

Sterling's approximation
 $\ln z! \approx z \ln z - z$

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$$S = -k \sum_l n_l \ln n_l + k \sum_l n_l \ln g_l + -k \sum_l n_l \ln N$$

$$S = k \left[\sum_l n_l \ln N + \sum_l n_l \ln g_l - \sum_l n_l \ln n_l \right]$$

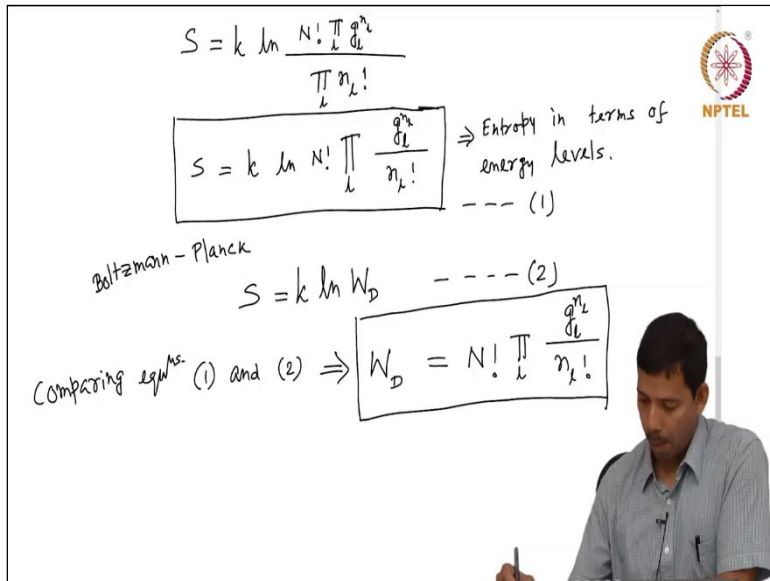
Adding and subtracting N

$$S = k \left[\sum_l n_l \ln N - N + N + \sum_l n_l \ln g_l - \sum_l n_l \ln n_l \right]$$

Sterling's approximation— $\ln x! = x \ln x - x$

$$S = k \left[\ln N! + \sum_l n_l \ln g_l - \ln \sum_l n_l! \right]$$

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$$S = k \ln \frac{N! \prod_l g_l^{n_l}}{\prod_l n_l!}$$

$$S = k \ln N! \prod_l \frac{g_l^{n_l}}{n_l!} \dots \dots \dots (1)$$

This is entropy in terms of energy levels.

So, now if you recall the Boltzmann Planck postulate of the relationship of entropy with the thermodynamic probability and there was the Boltzmann Planck postulate which we talked before.

$$S = k \ln W_D \dots \dots \dots (2)$$

So, Boltzmann Planck postulated that entropy is equal to $k \ln W$. So, write up is rather thermodynamic probability of the distinguishable particles k is the Boltzmann constant.

So comparing equations 1 and 2 what we kept is the expression for thermodynamic probability of the distinguishable particles in terms of the energy levels

$$W_D = N! \prod_l \frac{g_l^{n_l}}{n_l!}$$