

**Thermodynamics for Biological Systems:  
Classical and Statistical Aspects  
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**Lecture – 61  
Entropy in terms of Probability**

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$$\begin{aligned}
 & -Nk \sum p(\epsilon_i) \ln p(\epsilon_i) = ? & p(\epsilon_i) = \rho = \frac{e^{-\beta \epsilon_i}}{q} \\
 & = -Nk \sum p(\epsilon_i) \ln \frac{e^{-\beta \epsilon_i}}{q} \\
 & = +Nk \ln q + \beta Nk \sum \epsilon_i p(\epsilon_i) \\
 & = nk \ln q + \frac{Nk}{kT} \sum \epsilon_i \frac{n_i}{N} \\
 & = nk \ln q + \frac{N}{T} \cdot \frac{1}{N} \sum n_i \epsilon_i \\
 & = nk \ln q + \frac{E}{T} = S \Rightarrow \boxed{S = -nk \sum p_i \ln p_i}
 \end{aligned}$$

Now this is a very important relation so if I ask you what

$$-NK \sum_i \rho(\epsilon_i) \ln \rho(\epsilon_i) = ?$$

where Rho is the probability, which you have been defined before Rho on Rho. So, what does this expression correlate to how this expression or what this expression relate to what thermodynamic quantity as I had defined before Rho; again to remind you that this N and n they are the same thing and they are total number of particles.

$$\rho(\epsilon_i) \cong \rho = \frac{e^{-\beta \epsilon_i}}{q}$$

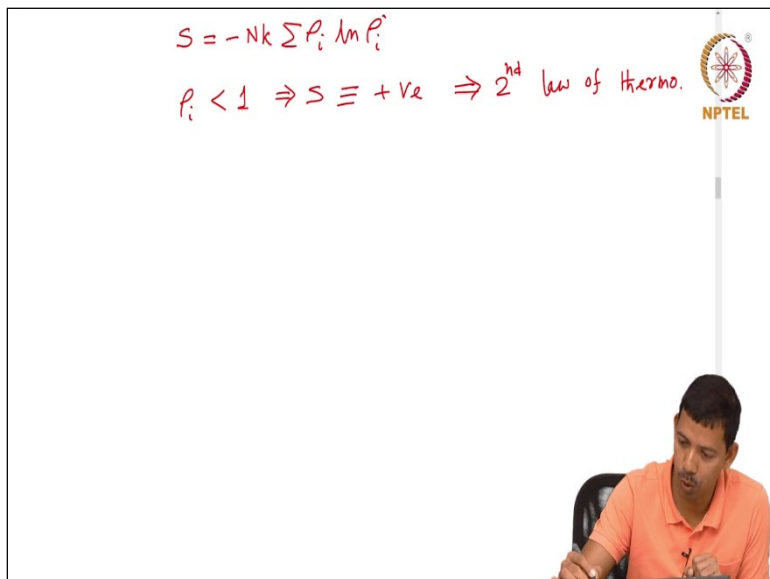
$$\begin{aligned}
 -NK \sum_i \rho(\epsilon_i) \ln \rho(\epsilon_i) &= -NK \sum_i \rho(\epsilon_i) \ln \frac{e^{-\beta \epsilon_i}}{q} \\
 &= +NK \ln q \sum \rho(\epsilon_i) + \beta Nk \sum \epsilon_i \rho(\epsilon_i) \\
 &= nk \ln q + \frac{NK}{kT} \sum \epsilon_i \frac{n_i}{N}
 \end{aligned}$$

$$= nK \ln q + \frac{E}{T} = S$$

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

So, therefore we write S is equal to - NK sum over Rho ln Rho. So now you look at here so this is a probability. So, probability is always less than 1 therefore this quantity the whole quantity will be positive and that is the second law of thermodynamics. Since probability is always less than 1. So, total quantity in the right-hand side will become positive and that implies that entropy of the system always increase and that is nothing but the second law of thermodynamic.

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So we got entropy is equal to -NK sum over Rho i ln Rho i now Rho i is the probability which is always less than 1 and if Rho i is always less than 1 what will be your entropy? Yes entropy will be positive and that is the second law of thermodynamics. The second law of thermodynamics that entropy of the system or randomness of the system increases, so again as you see that the probability is again a microscopic quantity can also explain the thermodynamic laws the basic thermodynamic laws.