Thermodynamics for Biological Systems: Classical and Statistical Aspects Prof. Sanjib Senapati Department of Biotechnology Indian institute of Technology - Madras

> Lecture – 65 Sackur -Tetrode Equation

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So, as you can see there is a difference of this n factorial term so therefore the entropy in terms of so therefore the entropy in terms of thermodynamic probability what we written Boltzmann Planck postulate was–

$$S = k \ln W_D$$

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$$S_{control} k lm \frac{W_D}{N!}$$

$$S = \frac{k lm W_D}{N!} + \frac{k lm W_D}{k!}$$

$$= \frac{k lm W_D}{N l} - k lm N!$$

$$= \frac{k lm W_D}{N} - k lm N! + \frac{k lm N}{l} + \frac{k lm N}{l!}$$

$$= \frac{k lm W_D}{N} + \frac{k lm N}{l!} + \frac{k lm N}{l!} + \frac{k lm N}{l!}$$

$$= \frac{k lm W_D}{N} + \frac{k lm lm N}{l!} + \frac{k lm N}{l!} + \frac{k lm N}{l!}$$

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So, that now needs to be re-written as-

$$S_{corrected} = k \ln \frac{W_D}{N!}$$

So, this is the corrected expression for entropy now, so previously is it was S is equal to k lon W rather W_D but since we have seen that distinguishable particles are over counted compared to the indistinguishable particles because of the n factorial term. So, therefore now in the next expression of entropy we divided k lon W_D by n factorial.

It can be re written as-

$$S = k \ln W_D - k \ln N!$$

$$S = Nk \ln q + \frac{E}{T} - Nk \ln N + Nk \text{ (applying sterlings appox.)}$$

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

For monoatomic gas system-

$$S = Nk \ln \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{V}{N} + \frac{5}{2} Nk$$

So, this expression of entropy is an experimentally verified corrected expression for entropy derived by Sackur and Tetrode the famous scientist.

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$$S = \frac{SackuY - Tetrode Equ^{h.}}{S = Nk \ln \left(\frac{2TmkT}{4^{t}}\right)^{3/2} \frac{V}{N} + \frac{5}{2}Nk \sqrt{n}$$

$$V \rightarrow 2V$$

$$N \rightarrow 2N \int S' = 2S$$

$$S' = 2Nk \ln \left(\frac{2TmkT}{4^{t}}\right)^{3/2} \frac{\mu V}{2N} + \frac{5}{2}(2N)k$$

$$S' = 2Nk \ln \left(\frac{2TmkT}{4^{t}}\right)^{3/2} \frac{\nu}{2N} + \frac{5}{2}(2N)k$$

$$= 2\left[Nk \ln \left(\frac{2TmkT}{4^{t}}\right)^{3/2} \frac{V}{N} + \frac{5}{2}Nk\right]$$

$$= 2S \Rightarrow Gibbs paradox is $2e solve$$$

Now let us check whether this corrected entropic expression could get rid of the gibbs paradox. So, now basically what we have to check is whether entropy is now showing has an extensive property.

So, we are increasing the volume V to 2V and we are increasing the number of particles N to 2N so we are basically doubling of the volume and number of particles of the system and therefore my new entropy is prime should become 2S because S is an extensive property. Let us see whether we are getting that?

$$S' = 2Nk \ln \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{2V}{2N} + \frac{5}{2} (2N)k$$
$$S' = 2[Nk \ln \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N} + \frac{5}{2} Nk]$$
$$S' = 2S$$

So, therefore this is 2S so therefore the Gibbs paradox is Gibbs paradox is resolved.