Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 66
Partition Function and Helmholtz and Gibbs Free Energy

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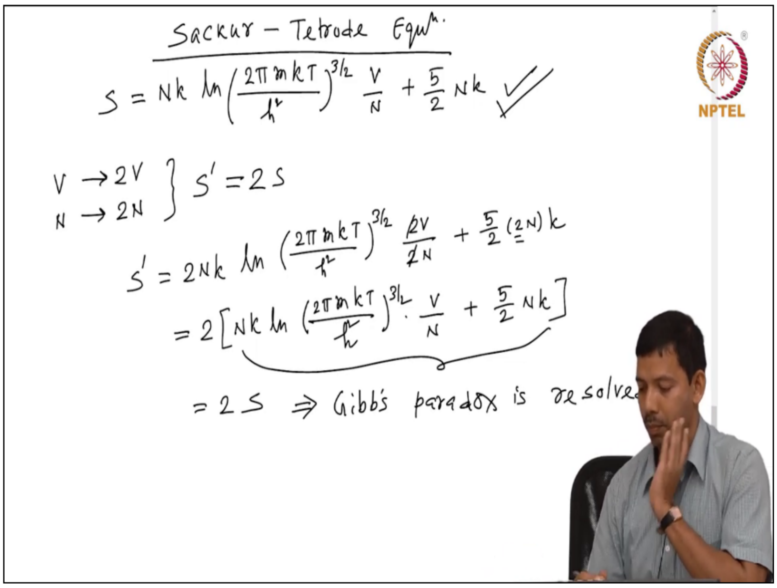

Sackur – Tetrode Eqn.

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

$$\left.\begin{matrix} V \rightarrow 2V \\ N \rightarrow 2N \end{matrix}\right\} S' = 2S$$

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

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

$= 2S \Rightarrow$ Gibb's paradox is resolve

So, now that we have resolved Gibb's paradox. Let us see how we can correlate the thermodynamic quantities other thermodynamic quantities like Gibbs free energy, Helmholtz free energy, chemical potential with the partition function.

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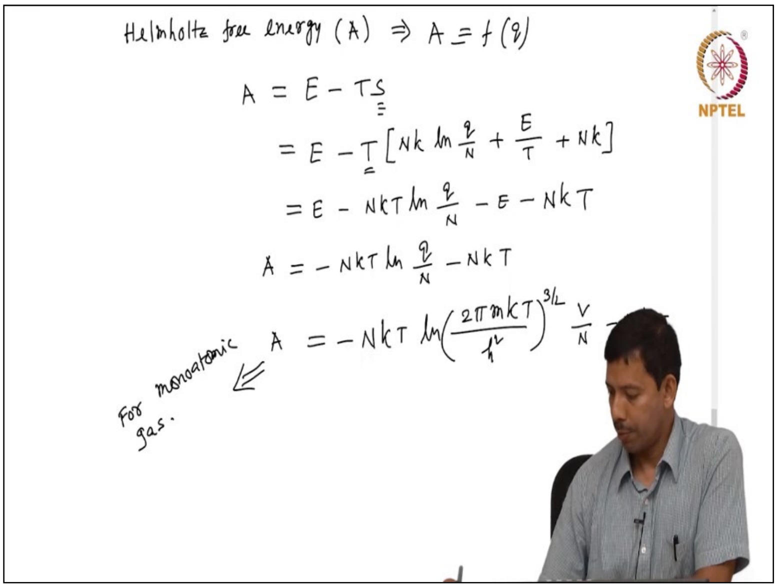

Helmholtz free energy (A) $\Rightarrow A = f(q)$

$$A = E - TS$$

$$= E - T\left[Nk\ln\frac{q}{N} + \frac{E}{T} + Nk\right]$$

$$= E - NkT\ln\frac{q}{N} - E - NkT$$

$$A = -NkT\ln\frac{q}{N} - NkT$$

$$A = -NkT\ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V}{N}$$

For monoatomic gas. $\Leftarrow$

So, let us talk first about the Helmholtz free energy as I recall that since we had a problem with the definition of thermodynamic probability. So, even though we got some expression for our quantities they might suffer the inaccuracy due to W and therefore you need to find out the corrected expression of the Thermodynamic quantity in terms of the partition function that is all final goal that if we know the partition function.

$$\text{Helmholtz energy (A)} \equiv \text{f(q)}$$

$$A = E - TS$$

$$A = E - T[Nk\ln\frac{q}{N} + \frac{E}{T} + nK]$$

$$\boldsymbol{A = -NkT\ln\frac{q}{N} - NkT}$$

For mono-atomic gas–

$$A = NkT\ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V}{N} - NkT$$

So we then calculate so partition function is a microscopic quantity and our goal is to correlate that microscopic quantity with the macroscopic properties part classical thermodynamics define. So, Helmholtz energy A is one such quantity and our goal would be now to see A as a function of q partition function.

So this is the expression of A for a special case of monatomic gas. So this is the expression for Helmholtz energy what is the expression for chemical potential?

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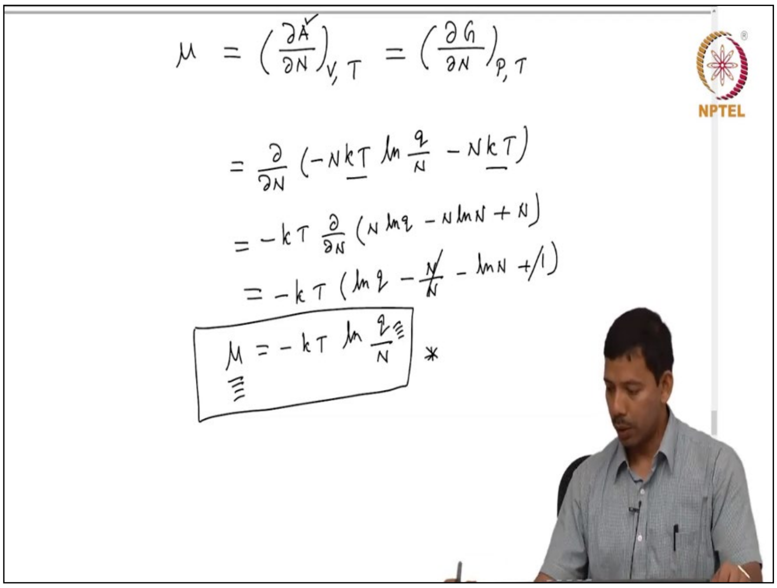

$$\mu = \left(\frac{\partial \cancel{A}}{\partial N}\right)_{V,T} = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

$$= \frac{\partial}{\partial N}\left(-NkT \ln\frac{q}{N} - NkT\right)$$

$$= -kT\frac{\partial}{\partial N}\left(N\ln q - N\ln N + N\right)$$

$$= -kT\left(\ln q - \frac{\cancel{N}}{\cancel{N}} - \ln N + \cancel{1}\right)$$

$$\boxed{\mu = -kT\ln\frac{q}{N}} \; *$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

$$= \frac{\partial}{\partial N}\left(-NkT\ln\frac{q}{N} - NkT\right)$$

$$\boldsymbol{\mu = -kT\ln\frac{q}{N}}$$

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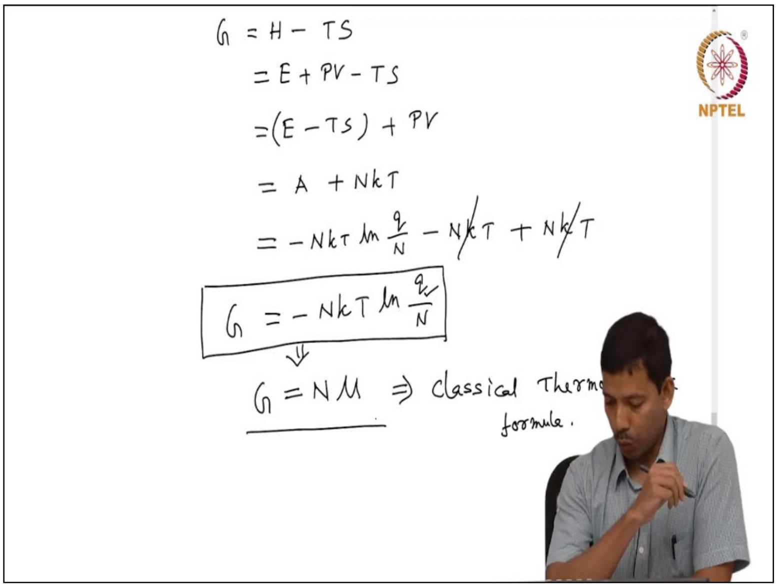

$$G = H - TS$$

$$= E + PV - TS$$

$$= (E - TS) + PV$$

$$= A + NkT$$

$$= -NkT\ln\frac{q}{N} - N\cancel{k}T + N\cancel{k}T$$

$$\boxed{G = -NkT\ln\frac{q}{N}}$$

$$\Downarrow$$

$$\underline{G = N\mu} \Rightarrow \text{Classical Therm}$$

formula.

So, another very important thermodynamic quantity is the Gibbs free energy.

$$G = H - TS$$

$$G = E + PV - TS$$

$$G = (E - TS) + PV$$

$$G = A + NkT$$

$$\boldsymbol{G = -NkT \ln \frac{q}{N} = N\mu}$$

So, G how is G related to the partition function.
So, it is the classical thermodynamic formula what you can also derive from statistical thermodynamics formulation.

So basically what we have seen so far is that if you have the understanding of quantum states quantum energy levels quantum definition of degeneracy then you can come up with different expressions which relate various thermodynamic quantities like free energy, chemical potential, entropy with the most important statistical thermodynamics quantity q the partition function.
So, since partition function basically tells how the particles are distributed over the different energy states and energy levels if you know how the particles are distributed which is a macroscopic information.

So from there we can always get you know the thermodynamic quantities like G H S from q and that is what we have derived so far. So, what is the way forward now from going from the quantum system to the biological system or you know molecular system where we have our system is much more complex than the small quantum system that we will see now.