Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 59
Relationship between Partition Function and Thermodynamic quantities

We have seen that partition function is one of the most important quantities in statistical thermodynamics. Now, let us see how partition function is related to various thermodynamic quantities.

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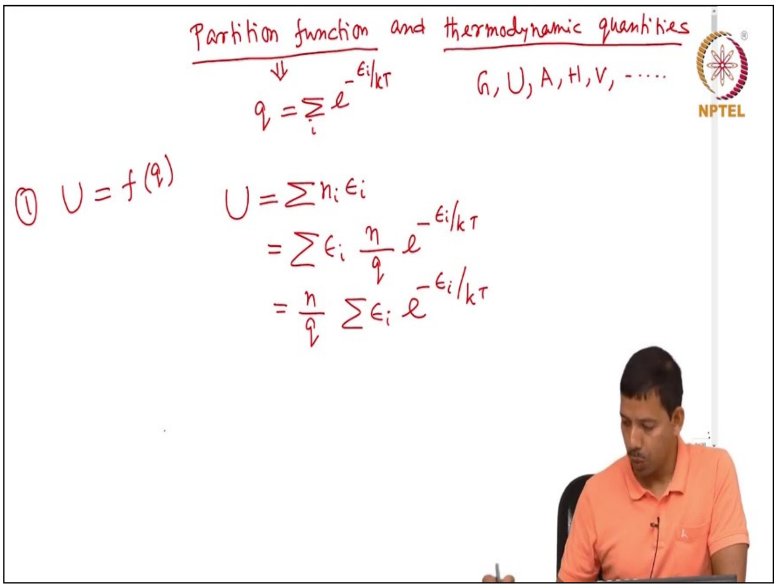

Partition function and thermodynamic quantities

$\Downarrow$

$q = \sum_i e^{-\epsilon_i/kT}$

G, U, A, H, V, - ....

① $U = f(q)$

$U = \sum n_i \epsilon_i$

$= \sum \epsilon_i \frac{n}{q} e^{-\epsilon_i/kT}$

$= \frac{n}{q} \sum \epsilon_i e^{-\epsilon_i/kT}$

The thermodynamic quantities for example G total energy, potential energy U, Helmholtz's free energy A, enthalpy H given volume and so on so forth are the thermodynamic quantities. So, today we are basically trying to link the microscopic q with the macroscopic quantities G U A H V and so on and so forth okay. So, to start with let us see the relationship between U the potential energy of the system, as a function of partition function. Thus the first relation between partition function and thermodynamic quantities will be negative.

We know that

$$q = \sum e^{-\frac{\varepsilon_i}{kT}}$$

and

$$U = f(q)$$

$$U = \sum_i n_i \varepsilon_i$$

$$U = \frac{n}{q} \sum_i \varepsilon_i \, e^{-\frac{\varepsilon_i}{kT}}$$

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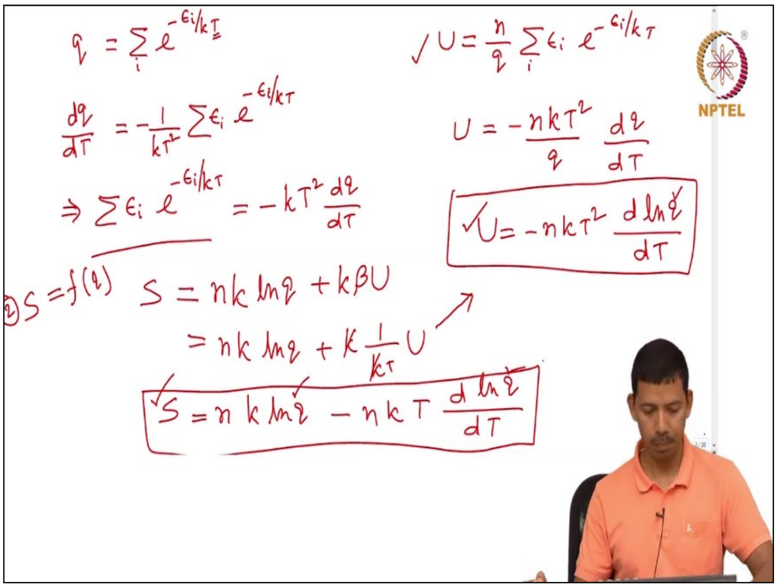

$$q = \sum_i e^{-\epsilon_i/kT}$$

$$\frac{dq}{dT} = -\frac{1}{kT^2} \sum \epsilon_i \, e^{-\epsilon_i/kT}$$

$$\Rightarrow \sum \epsilon_i \, e^{-\epsilon_i/kT} = -kT^2 \frac{dq}{dT}$$

$$✓ \; U = \frac{n}{q} \sum_i \epsilon_i \, e^{-\epsilon_i/kT}$$

$$U = -\frac{nkT^2}{q} \frac{dq}{dT}$$

$$\boxed{✓ \; U = -nkT^2 \frac{d \ln q}{dT}}$$

$$② \; S = f(q) \quad S = nk \ln q + k\beta U$$

$$= nk \ln q + k \frac{1}{kT} U$$

$$\boxed{✓ \; S = nk \ln q - nkT \frac{d \ln q}{dT}}$$

$$q = \sum e^{-\frac{\varepsilon_i}{kT}}$$

$$\frac{dq}{dT} = -\frac{1}{kT^2} \sum \varepsilon_i \, e^{-\frac{\varepsilon_i}{kT}}$$

Hence

$$\sum \varepsilon_i \, e^{-\frac{\varepsilon_i}{kT}} = -kT^2 \frac{dq}{dT}$$

As

$$U = \frac{n}{q} \sum_i \varepsilon_i \, e^{-\frac{\varepsilon_i}{kT}}$$

$$U = \frac{-nkT^2}{q} \frac{dq}{dT}$$

$$\boldsymbol{U = -nkT^2 \frac{d \ln q}{dT}}$$

Here, U is potential energy, q is partition function, n total number of particles in the system and k is Boltzmann constant.

2) Entropy (S)

$$S = f(q)$$

$$S = nk\ln q + k\beta U$$

By putting the value of ($\beta = 1/kT$) and U from the above equation we get

$$\boldsymbol{S = nk\ln q - nkT\,\frac{d\ln q}{dT}}$$

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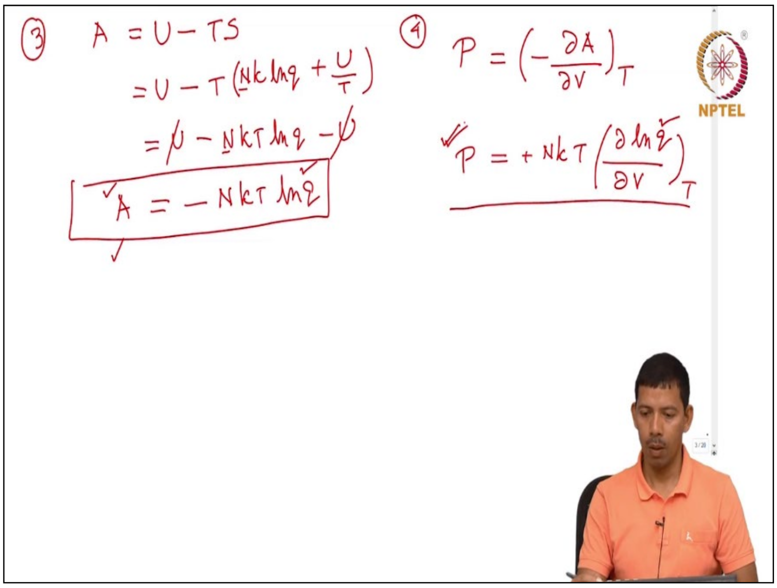

③ $A = U - TS$

$= U - T\left(Nk\ln q + \frac{U}{T}\right)$

$= \cancel{U} - NkT\ln q - \cancel{U}$

$\boxed{A = -NkT\ln q}$

④ $P = \left(-\frac{\partial A}{\partial V}\right)_T$

$P = +NkT\left(\frac{\partial \ln q}{\partial V}\right)_T$

3) Helmholtz energy (A)

$$A = U - TS$$

$$A = U - T\left(Nk\ ln\ q + \frac{U}{T}\right)$$

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

4) Pressure (P)

$$P = \left(-\frac{\partial A}{\partial V}\right)_T$$

$$\boldsymbol{P = NkT\,(\frac{\partial \ln q}{\partial V})_T}$$

This is the expression for P in terms of partition function q.

So, essentially all these expressions are saying that if you can somehow get the partition function, if you can calculate the partition function, or how the particles are distributed at constants in the states then you can easily get all the thermodynamic quantities of your interest,
Okay. So, these are some general relationship. Now, let us take a special case. And for and in in here, we will be finding out the partition function of a monoatomic gas, so that is our next topic.