Fundamentals of Statistical Thermodynamics

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Lecture – 20

Relating Canonical Partition Function Internal Energy and Entropy

Welcome back. Now that we have introduced the concepts of ensembles and we have already talked about canonical partition function. Therefore, we must relate the canonical partition function with different thermodynamic quantities. And later on, we will discuss that how to recover the molecular partition function from canonical partition function and then we will discuss that how this link between individual molecular properties and bulk thermodynamic properties is justified. In the previous lecture, we talked about canonical partition function which is $\sum_i e^{-\beta E_i}$. This E_i is a energy state E_i in which n_i that special character n_i number of members they belong to.

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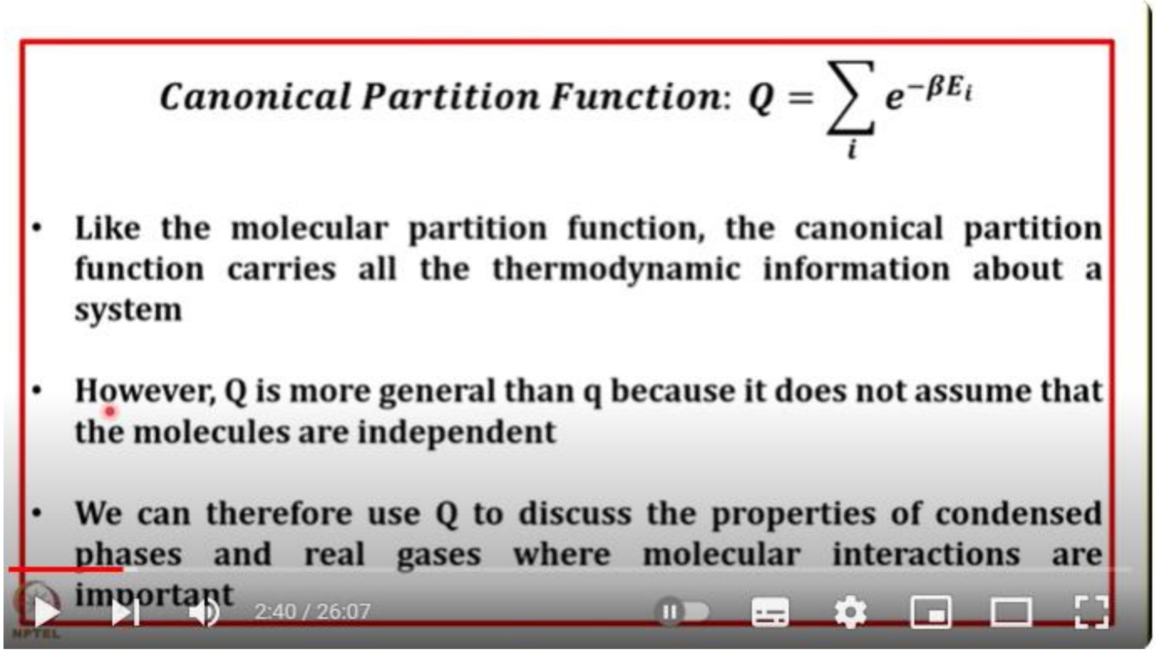

Canonical Partition Function: $Q = \sum_i e^{-\beta E_i}$

- **Like the molecular partition function, the canonical partition function carries all the thermodynamic information about a system**
- **However, Q is more general than q because it does not assume that the molecules are independent**
- **We can therefore use Q to discuss the properties of condensed phases and real gases where molecular interactions are important**

Like molecular partition function, molecular partition function we gave the symbol small q. So, like the molecular partition function, this canonical partition function carries all the thermodynamic information about a system. That means we can connect this q with various thermodynamic quantities. However, look at the comment.

Canonical partition function is more general than molecular partition function because it does not assume that the molecules are independent. Keep that in mind. Therefore, we can use canonical partition function to discuss the properties of even condensed phases and real gases where molecular interactions are important. Here you can recall the different ensembles. For example, canonical ensemble in which n, v, t are fixed and energy is changed.

But basically what is being tried to say here is that we can now use this concept of canonical partition function to describe, to discuss the properties of condensed phases and real gases, not ideal gases, real gases, the gases which deviate from ideality. Why do the gases deviate from ideality? Because of the onset of intermolecular interactions. And what is important in condensed phase? That means when the molecules interact more, they can even go to liquid phase or solid phase. So, therefore, a discussion on canonical partition function allows you to discuss the properties of condensed phases that is liquid and solids and also the systems like gases in which the intermolecular interactions operate. Now let us start developing some relations.

We have talked about the total energy of the ensemble as this special character of E. And the total number of members as this special character n. So obviously the energy of one system or one member of the ensemble is going to be an average. This is the average energy of one member of the ensemble. It is going to be E divided by n.

And we know that U minus U(0) is equal to E. U is equal to U(0) plus E that is applying to one member of the ensemble. And this equation is rewritten now in this form. U is equal to U(0) plus the total energy of the ensemble and the total number of members in the ensemble. What is this E is equal to the total energy of the entire ensemble. This can be written as I number of members in an energy state, I divided by I am retaining that n. This is equal to what? This is equal to summation I population of the members in i^{th} state which is equal to n I by n and inside we have I. Remember that n I upon n which is equal to the fractional population of i^{th} level is equal to exponential minus βE_i by Q. You are expressing in terms of the canonical partition function. So that means I can write E is equal to summation I instead of p_i.

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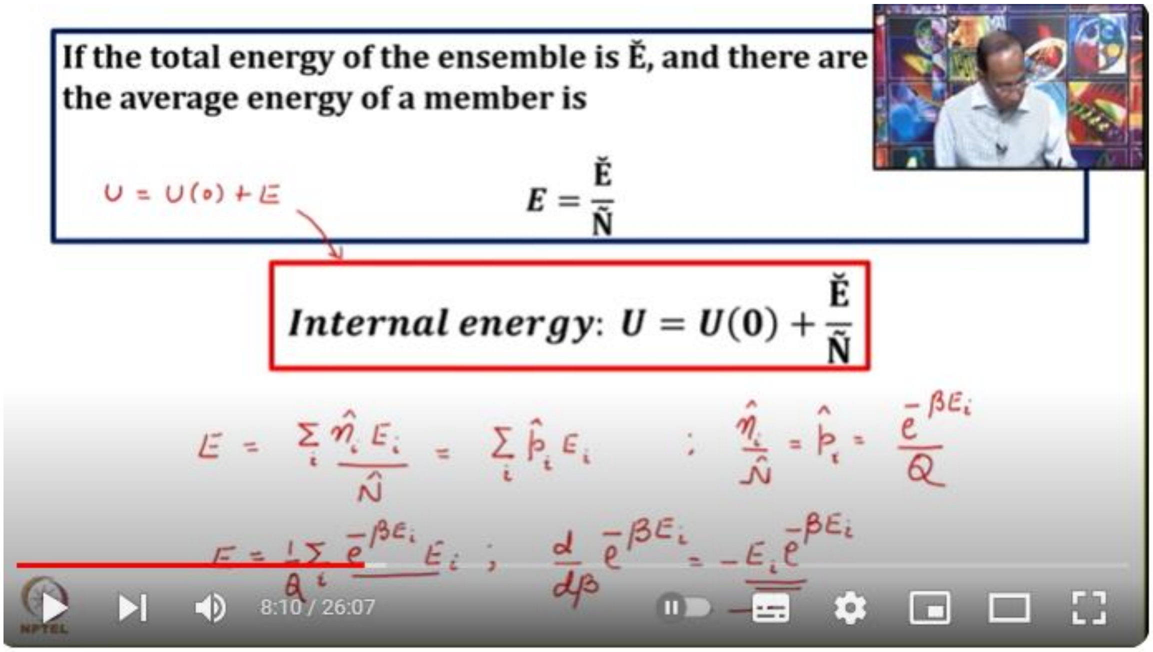

If the total energy of the ensemble is Ě, and there are
the average energy of a member is

$U = U(0) + E$

$$E = \frac{\check{E}}{\tilde{N}}$$

$$\boxed{\textit{Internal energy}:\ U = U(0) + \frac{\check{E}}{\tilde{N}}}$$

$$E = \frac{\sum_i \hat{n}_i E_i}{\hat{N}} = \sum_i \hat{p}_i E_i \quad ; \quad \frac{\hat{n}_i}{\hat{N}} = \hat{p}_i = \frac{e^{-\beta E_i}}{Q}$$

$$E = \frac{1}{Q}\sum_i \underline{e^{-\beta E_i} E_i} \ ; \quad \frac{d}{d\beta} e^{-\beta E_i} = \underline{\underline{-E_i e^{-\beta E_i}}}$$

I will write exponential minus βE_i. There is another E I over there and there is one over q. So, we will use the same method as we used earlier in the derivation for expression which connects u and q molecular partition function. What we do is we will consider d d β of exponential minus βE_i. Let us consider this.

This is equal to minus E_i into exponential minus βE_i. So now this can be put over here. So, what we have? Let us discuss that. We had E is equal to minus 1 by Q into d d β of summation I exponential minus βE_i. This comes from when you substitute exponential E I into exponential minus βE_i.

This is basically minus of this derivative and when you put this minus of this derivative this derivative into this it results into this expression. So therefore, what we have? E is nothing but U - U(0)is equal to minus 1 by q into del q del β at constant volume. We have got this from this expression. We just express U is equal to U(0) plus summation I p_i E_i and then p I we expressed in terms of 1 by q and Ei exponential minus βE_i and then we consider the derivative of exponential minus βE_i we arrive at this expression. U-U(0)is equal to minus 1 by q del q by del β at constant volume.

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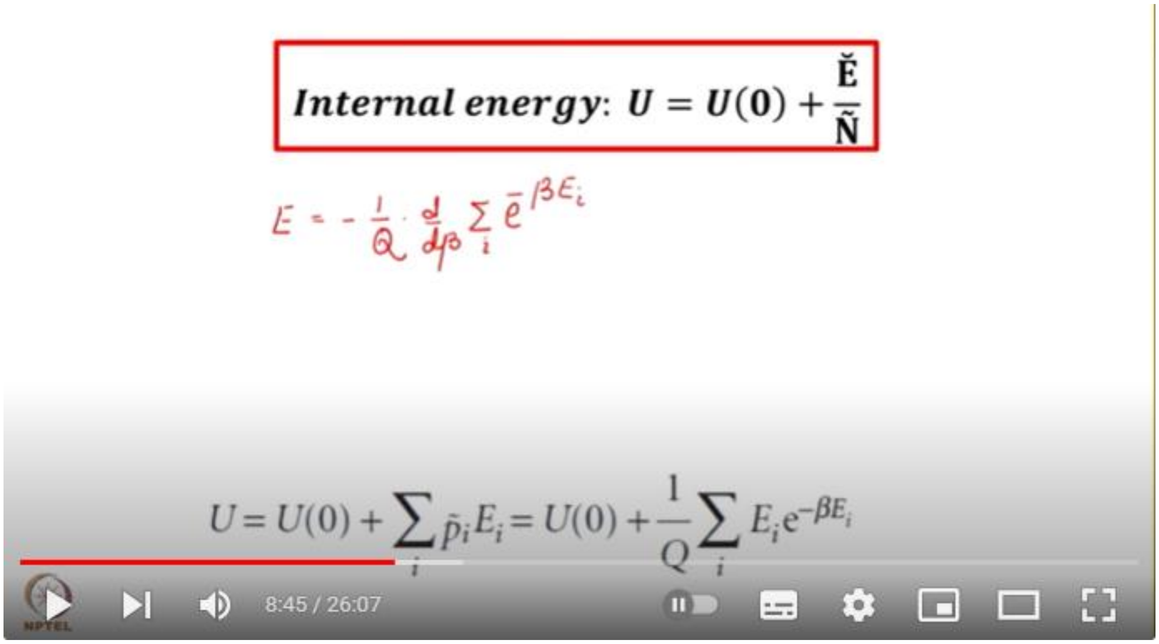

Internal energy: $U = U(0) + \frac{\breve{E}}{\tilde{N}}$

$$E = -\frac{1}{Q} \cdot \frac{d}{d\beta} \sum_i \bar{e}^{\beta E_i}$$

$$U = U(0) + \sum_i \tilde{p}_i E_i = U(0) + \frac{1}{Q} \sum_i E_i e^{-\beta E_i}$$

This is for canonical example. So once again from using u is equal to u 0 plus summation I p I and so on we have this expression U – U (0) is equal to minus 1 by q del q del β at constant volume. You can also use this as U – U (0) consume q with d q and you can write minus del log q del β at constant volume. This is what is written over here that u is equal to u 0 minus 1 by q del q del β at constant volume or U (0) minus del log q by del β at constant volume. So, what is the significance of this equation whether you use this equation or this equation? What is the significance? Earlier you remember that when we talked about the molecular partition function there U – U (0) was equal to minus n by q del q by del β at constant volume that q was molecular partition function.

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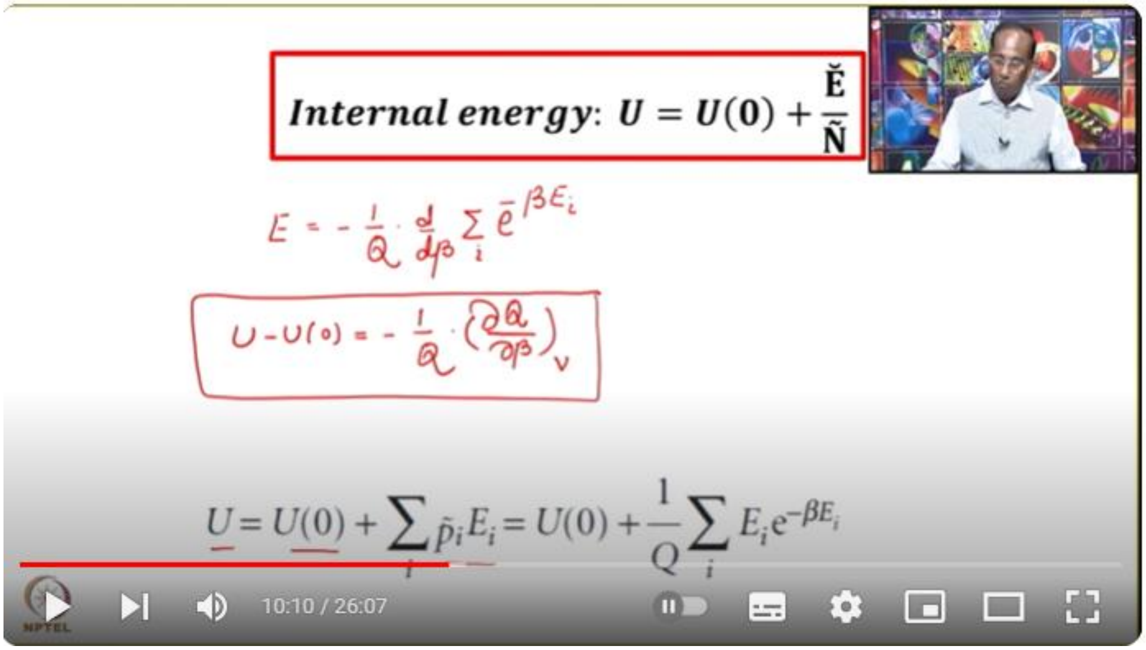

Internal energy: $U = U(0) + \frac{\breve{E}}{\tilde{N}}$

$$E = -\frac{1}{Q}\cdot\frac{d}{d\beta}\sum_i \bar{e}^{\beta E_i}$$

$$\boxed{U - U(0) = -\frac{1}{Q}\cdot\left(\frac{\partial Q}{\partial \beta}\right)_V}$$

$$\underline{U} = \underline{U(0)} + \sum_i \tilde{p}_i E_i = U(0) + \frac{1}{Q}\sum_i E_i e^{-\beta E_i}$$

Here we have canonical partition function. The advantage of canonical partition function uses here is as I just discussed earlier that here you can incorporate intermolecular interactions. Here you can use such treatment to discuss condensed systems. You can treat such you can use such treatment in discussing non ideality. Whether you use this equation or you use this equation we have to know how this canonical partition function is related to molecular partition function.

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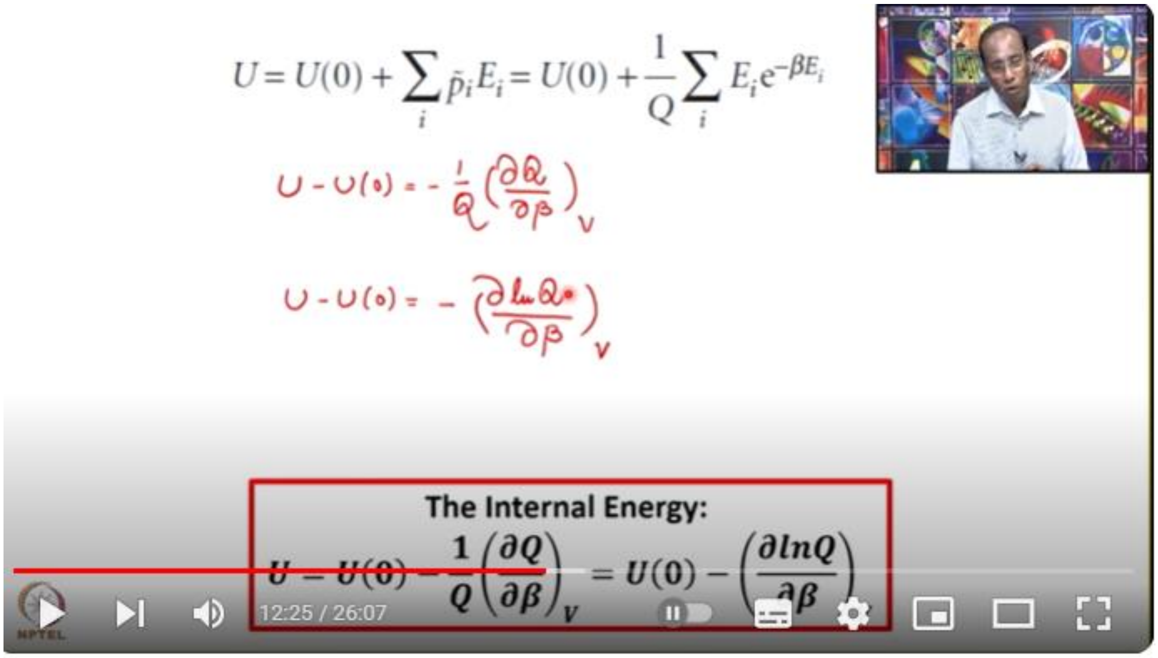

$$U = U(0) + \sum_i \tilde{p}_i E_i = U(0) + \frac{1}{Q}\sum_i E_i e^{-\beta E_i}$$

$$U - U(0) = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_v$$

$$U - U(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_v$$

The Internal Energy:

$$U = U(0) - \frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V = U(0) - \left(\frac{\partial \ln Q}{\partial \beta}\right)$$

We need to develop that connection. Let us move towards that, but before that let us connect entropy with canonical partition function. By now we have introduced the total weight of a configuration and if we need to connect this total weight of a configuration with weight of each member, note the difference between the total weight of configuration and weight of each member. How they are related? They are related by this expression. The total weight of a configuration of the ensemble is the product of average weight w of each member.

So, there are total n members. So, therefore, it will be w raise to the power this special character n. How this is how they are related? All right. So, that means the weight of or the average weight of each member of the ensemble I can write as the overall weight total weight of the configuration of the ensemble raise to the power 1 by n and we have already derived s is equal to k log w. We have derived this expression where this w that we have written here is with log is the weight of one system weight of a configuration in when we apply to that one system.

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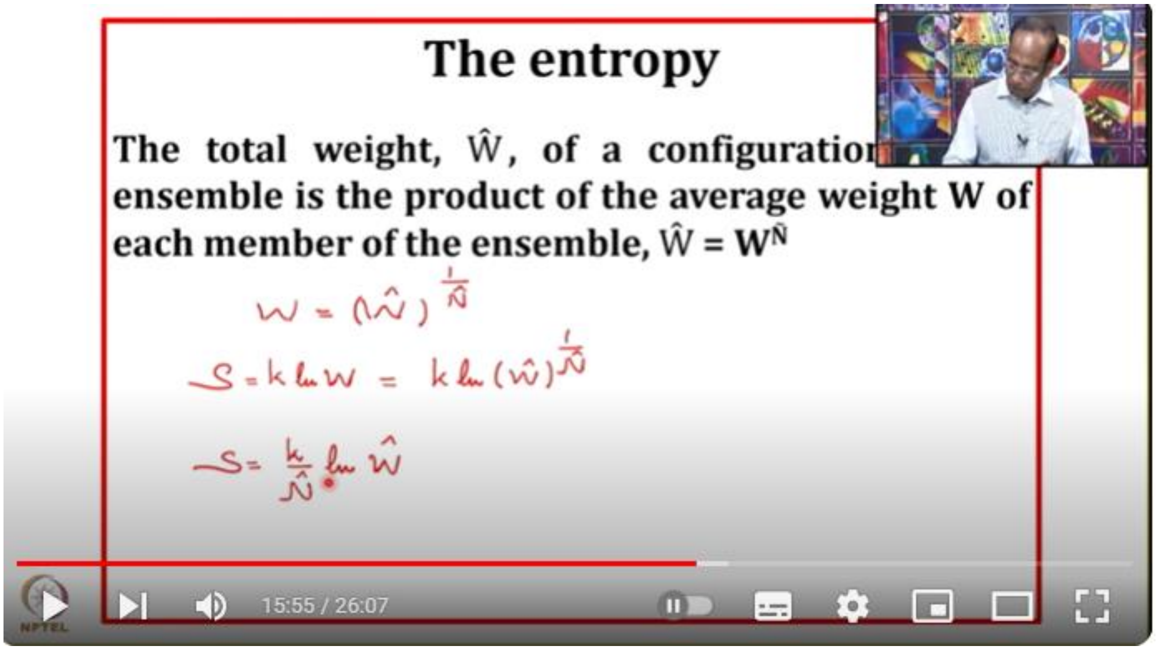

The entropy

The total weight, Ŵ, of a configuratio ensemble is the product of the average weight W of each member of the ensemble, Ŵ = W$^{\hat{N}}$

$$W = (\hat{W})^{\frac{1}{\hat{N}}}$$

$$S = k \ln W = k \ln (\hat{W})^{\frac{1}{\hat{N}}}$$

$$S = \frac{k}{\hat{N}} \ln \hat{W}$$

Let us apply substitute now k log instead of w I will write this special w raise to the power 1 by n or in other words I have s is equal to k by n log w. Now we have written the entropy in terms of the properties of ensemble the total number of members in ensemble and the total weight of a configuration of the ensemble and the rest of the treatment now is same as that we did for the molecular partition function. We wrote some expression for log w in terms of you know $nlogn - \sum_i n_i \log n_i$ the same treatment is to be done for not repeating the same thing I am skipping those steps and will write the final expression for entropy and its connection with molecular partition function. So, what we have here is s is equal to k log w and when we connect with this, we come up with this expression k by n log w and as I said that now using the same methodology that we adopted earlier eventually you get a relationship between entropy and canonical partition function. We have just connected internal energy with the canonical partition function and the additional term here that comes is k log q.

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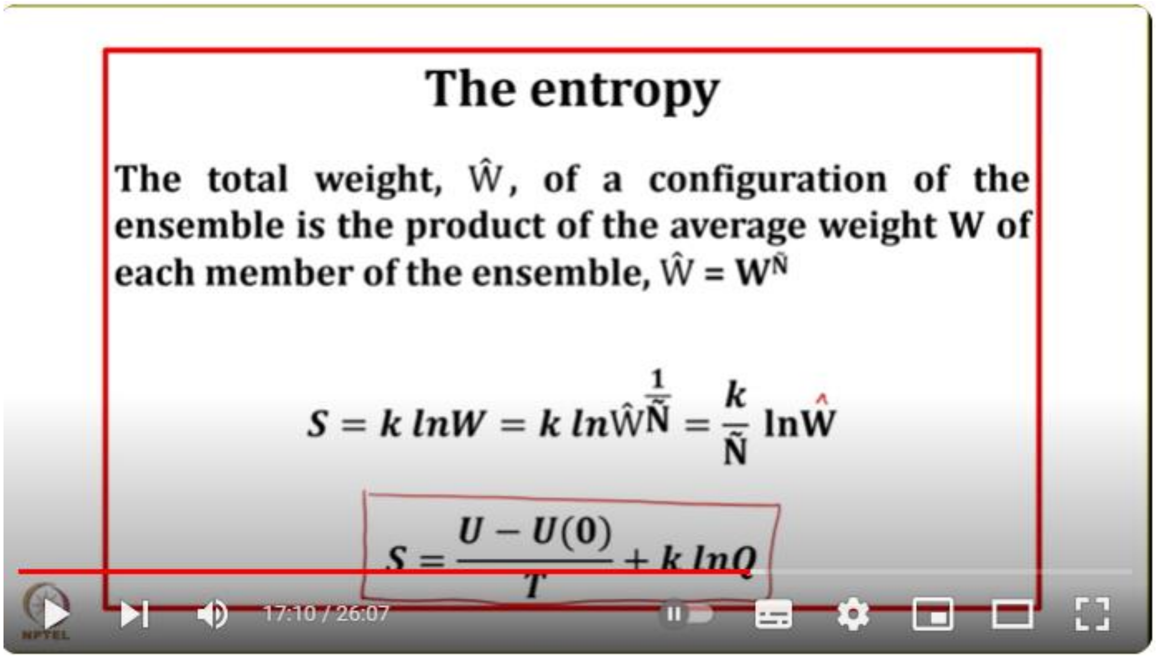

The entropy

The total weight, $\hat{W}$, of a configuration of the ensemble is the product of the average weight W of each member of the ensemble, $\hat{W} = W^{\tilde{N}}$

$$S = k\ln W = k\ln \hat{W}^{\frac{1}{\tilde{N}}} = \frac{k}{\tilde{N}}\ln\hat{W}$$

$$\boxed{S = \frac{U-U(0)}{T} + k\ln Q}$$

So, this is a more general representation of thermodynamic quantities which are connected with the more general representation of the examples for example here we are discussing the canonical ensemble. Remember the earlier discussion when we connected entropy with molecular partition function that time, we used U – U (0) by T plus n k log q and U-U (0) was minus n del log q by del β at constant volume. These expressions were used for molecular partition function and the molecules were not allowed to interact with each other. Here we have a more general expression between entropy and canonical partition function in which as we just discussed that you allow the interactions. Now the question is that will this relation turn out to be the same as this relation when we consider recovering molecular partition from the canonical partition function.

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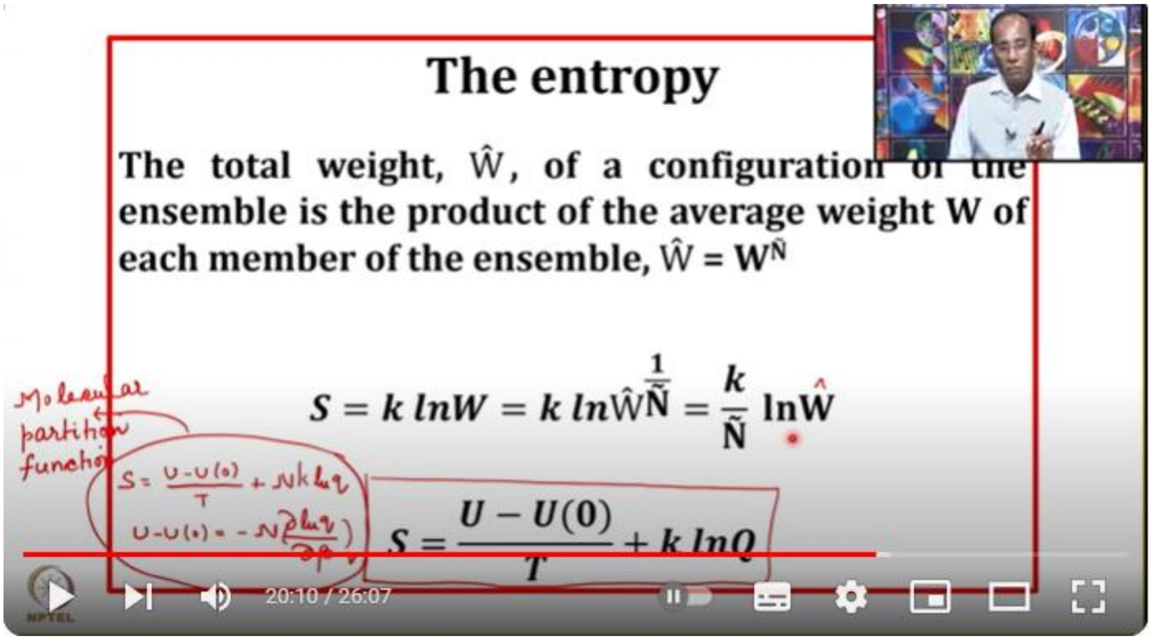

The entropy

The total weight, $\hat{W}$, of a configuration of the ensemble is the product of the average weight W of each member of the ensemble, $\hat{W} = W^{\tilde{N}}$

$$S = k\,lnW = k\,ln\hat{W}^{\frac{1}{\tilde{N}}} = \frac{k}{\tilde{N}}\ln\hat{W}$$

$$\boxed{S = \frac{U - U(0)}{T} + k\,lnQ}$$

Molecular partition function

$$S = \frac{U-U(0)}{T} + Nk\ln q$$

$$U-U(0) = -N\left(\frac{\partial \ln q}{\partial \beta}\right)$$

The recovery of molecular partition function from canonical partition function we need to bring in distinguishable and non-distinguishable molecules. Therefore, when we connect this canonical partition function with the molecular partition function the overall resulting equation may or may not be same that we got in case of molecular partition function. Remember although we have skipped many steps in this particular case differentiate between the weight of configuration of the ensemble and the average weight of one member of the ensemble how they are connected with each other. And then when you substitute in this you come up with a logarithmic term. Now this logarithmic term in the case of molecular partition function remember I highlighted that logW which is equal to $nlogn - \sum_i n_i \log n_i$

Only here when you expand this log w in terms of $nlogn - \sum_i n_i \log n_i$ there you will be talking about the number of members of the ensemble which are there i n_i thstate. Talking about the applications of the canonical ensemble concept the thermodynamic quantities that we are going to connect with the molecular partition function from now onwards what we will do is we will first develop a relationship between the thermodynamic quantity and canonical partition function. And then we will see that how the canonical partition function when translates or when converted into molecular partition function and what type of relationship it takes. So, therefore, when we have this independent molecules when they are identifiable when they are distinguishable and when they are indistinguishable then how to connect this molecular partition function with canonical partition function that is going to be the matter of discussion in our next lecture. But looking back we have now connected the internal energy with the canonical partition function remember this significance of this expression.

What is internal energy? Internal energy is the sum of total energy of the system added up in all the forms and that total energy of the system added up in all the forms also includes the interaction energy. And therefore, this equation becomes very very important when you apply to condensed phases or when you apply to the real systems or non-ideal systems. And since this equation is carried over to the connection of entropy with canonical partition function via U - U(0) by T which is also connected to canonical partition function that means that interaction energy now is captured into this term and that is going to make difference over here. Obviously, there is another term which is coming over here because we will see that how this capital Q that is the canonical partition function is connected to molecular partition function which is small q. Now when we talk about switching over from perfect gases ideal gases or ideal systems to condensed phases to non-ideal system that is the real gases again and again, I am emphasizing on that the molecular interactions play important role over here whether the interactions are attractive interactions or these interactions are repulsive interactions.

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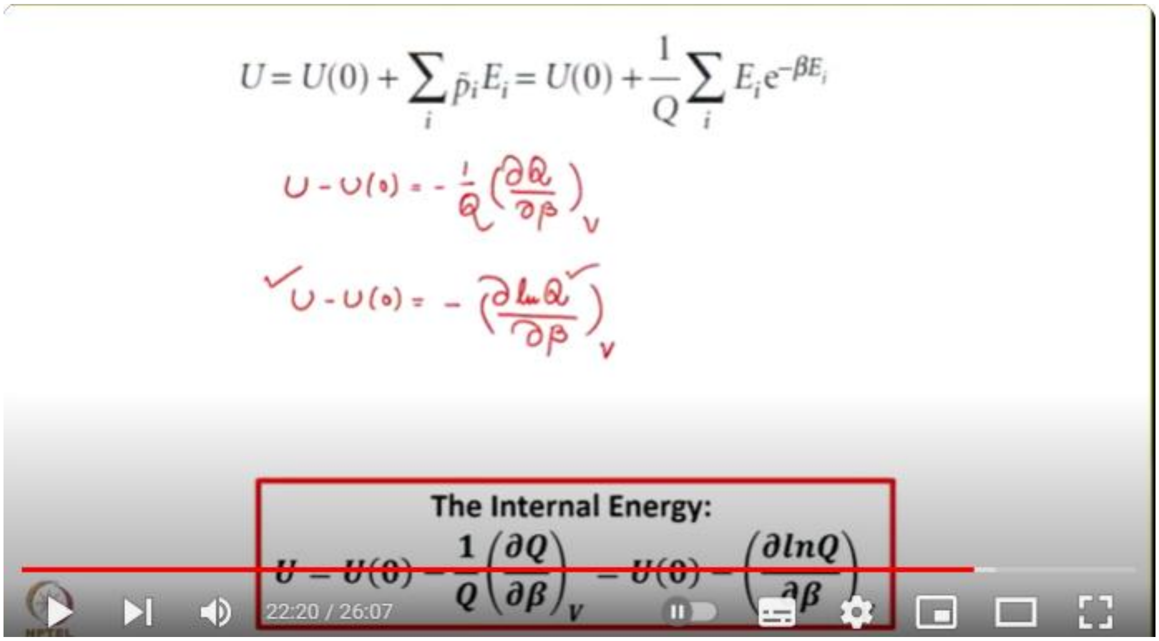

$$U = U(0) + \sum_i \tilde{p}_i E_i = U(0) + \frac{1}{Q}\sum_i E_i e^{-\beta E_i}$$

$$U - U(0) = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V$$

$$✓\; U - U(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V$$

The Internal Energy:

$$U - U(0) = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V \qquad U - U(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

Experimentally several thermodynamic quantities can reflect on the nature of intermolecular interactions. One such quantity is free energy of mixing, enthalpy of mixing, volume of mixing, entropy of mixing. And since we have here now derived expression for S, we have derived expression for U if you go back to the concepts of chemical thermodynamics changes in U changes in S can be connected to other thermodynamic quantities. For example, the changes in Gibbs free energy or the changes in enthalpy. So, therefore, developing such equations permit us to further develop equations for the changes in Gibbs free energy or changes in enthalpy and then bring in the non-ideality into this calculate or spectroscopically measure that and then compare with the other experimentally determined same thermodynamic quantities.

So, our next goal in the next lecture is going to be connecting canonical partition function with molecular partition function. We will see whether the connection remains same or it is different when the molecules are distinguishable or when the molecules are indistinguishable. We will discuss all these matters in the next lecture. Thank you. Thank you.