Fundamentals of Statistical Thermodynamics

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Lecture – 14

Connecting partition function with entropy

In this lecture, we are going to connect entropy with the molecular partition function. After having established a relationship between entropy and w, the weight of the most probable configuration, that is, we talked about S is equal to k log w. Now, we have to look out for the ways, that is, how to connect this log w with the molecular partition function. That is going to be our next goal. Now, let us refer back to our earlier discussion. When we talk that instead of w, it is better to talk in terms of log w because it will allow us to develop further relations, further relations in a more easier way and today the time has come to demonstrate that. Remember that log w is equal to n log n minus summation i n_i log n_i. This we have derived some time ago. Now, let us write, rewrite in some other way. Instead of n, let me write summation n i because n is equal to summation n_i.

Then, I have log n and I have minus summation i n_i log n_i and let us substitute S is equal to k log w.

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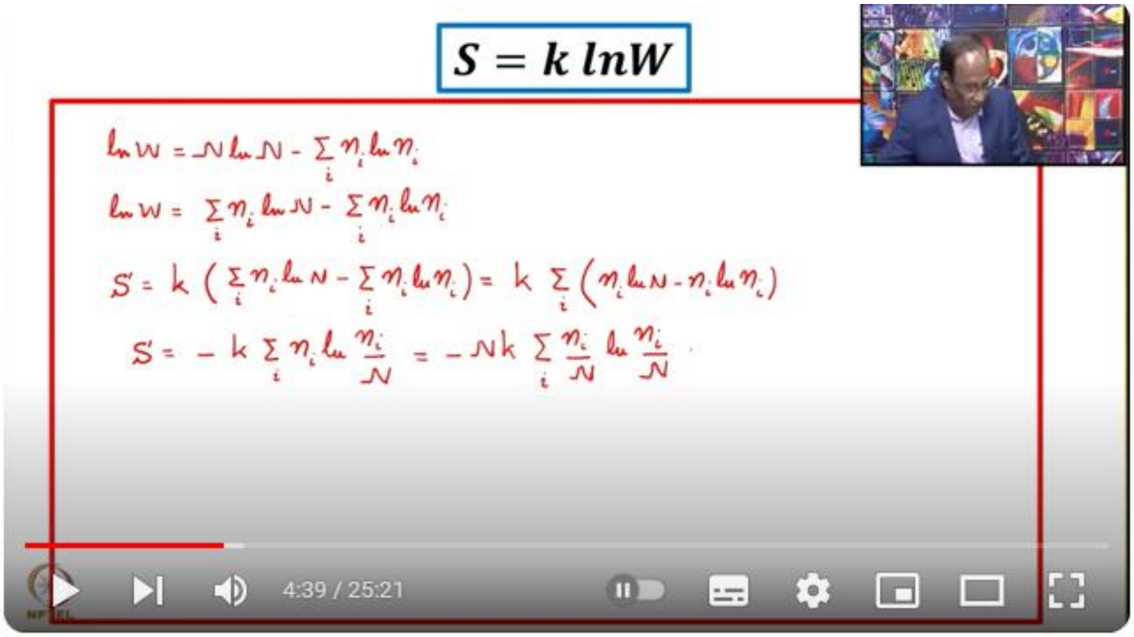

$$S = k\,lnW$$

$$\ln W = N\ln N - \sum_i n_i \ln n_i$$

$$\ln W = \sum_i n_i \ln N - \sum_i n_i \ln n_i$$

$$S = k\left(\sum_i n_i \ln N - \sum_i n_i \ln n_i\right) = k\sum_i \left(n_i \ln N - n_i \ln n_i\right)$$

$$S = -k\sum_i n_i \ln \frac{n_i}{N} = -Nk\sum_i \frac{n_i}{N} \ln \frac{n_i}{N}$$

So, instead of log w, write, let us write summation i n_i log n $_i$ minus summation i n $_i$ log n $_i$, which I can write as k summation i. Let me write i n $_I$ log n minus in $_I$ log n $_i$ Let us rewrite this. I can write this as minus k summation i n $_i$ log n $_i$ upon N

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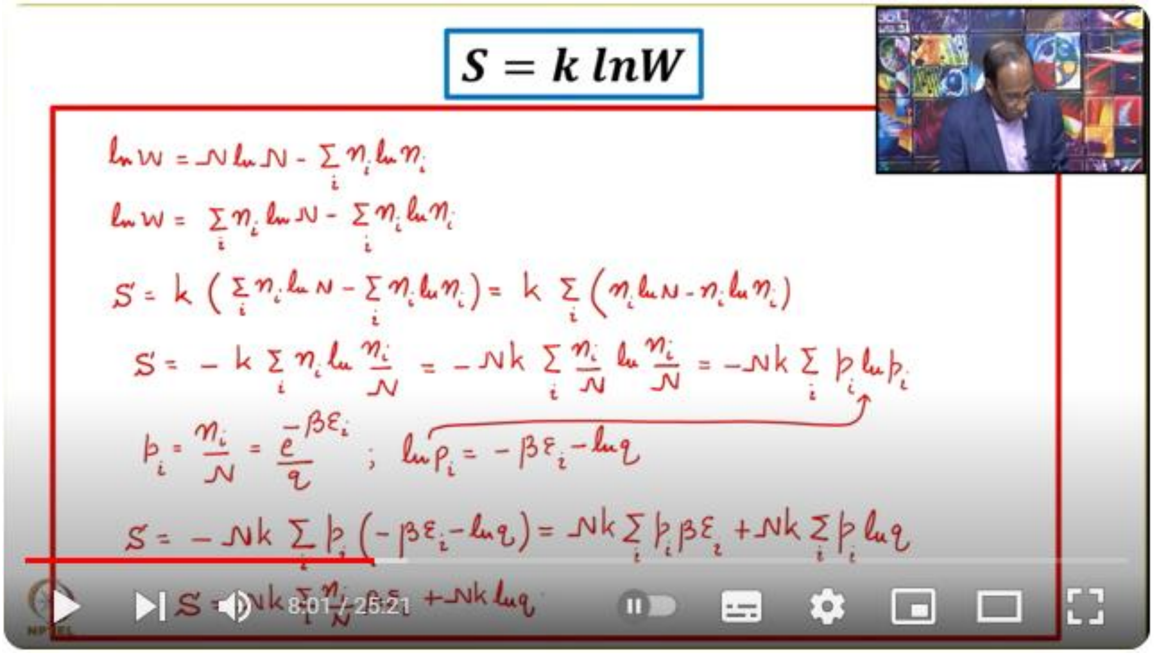

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$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{q} \; ; \; \ln p_i = -\beta\varepsilon_i - \ln q$$

$$S = -Nk \sum_i p_i\left(-\beta\varepsilon_i - \ln q\right) = Nk \sum_i p_i \beta\varepsilon_i + Nk \sum_i p_i \ln q$$

$$S = Nk \sum_i \frac{n_i}{N} \beta\varepsilon_i + Nk \ln q$$

I have brought the negative sign here because I am keeping this n $_i$ into the numerator. I will do one modification over here. I will multiply by n and divide by n here n_i upon N and I have log n $_i$ upon N. What is this n_i upon N ? It is the fractional population. You see the strategy over here.

We have converted S is equal to k log w into an expression, which relates entropy with fractional population. So, let us write this as minus n times K summation i. This is p_i log p_i. We have connected entropy with the fractional population of i n star. Why we have done this? Because we already know that a relationship exists between the fractional population of ith state and molecular partition function.

What is that? Remember that p_i is equal to n_i upon N, which is equal to exponential minus β e $_i$ upon q. We are moving towards connecting S with q. If p_i is this, then log p_i, this is what we are interested in log p_i is equal to minus β e_i minus log q. Now, I can substitute this p log p_i over here. Let us do that and see what happens.

So, I have S is equal to minus n times K summation i p_i and log p_i is minus β e $_i$ minus log q. We can now further work on this. This is equal to minus n minus becomes plus. So, n times K summation i p_i is equal to minus p_i β e $_i$, then plus n times K summation i p_i log q. We can further work on this.

Now, S is equal to here n K summation p_i β e $_i$. Let us try to now rewrite p_i as n_i upon N because that will allow me to further simplify this. So, this is going to be n times K summation i instead of p i, let me write n i upon N β e_i plus n K log q summation i p_i. We can further work on this. n and n get cancelled and β e i is equal to minus β is equal to 1 by K T.

I once again repeat this n and this n get cancelled. B is equal to 1 over K T. So, therefore, what I have is 1 by T summation i n $_i$ e $_i$ plus 1 by K T plus n K log q. I repeat what I have done. n and n get canceled. B is equal to 1 by K T. So, what I have is 1 by T, and inside we have n i and e_i left over and n K log q because summation of all the populations, fractional populations has to be equal to 1. So, log q is constant. I take it out of summation. So, summation i p_i, it is the sum of all fractional populations that has to be equal to 1.

So, I have this expression. Now, we have to now work upon this and let us now see what form it takes. Remember that this will be equal to I have summation n i e i. This is equal to total energy. This is total energy by T plus n K log q.

I will come back to this later on. Summation n_i e $_i$ is equal to total energy by T plus n k log q.

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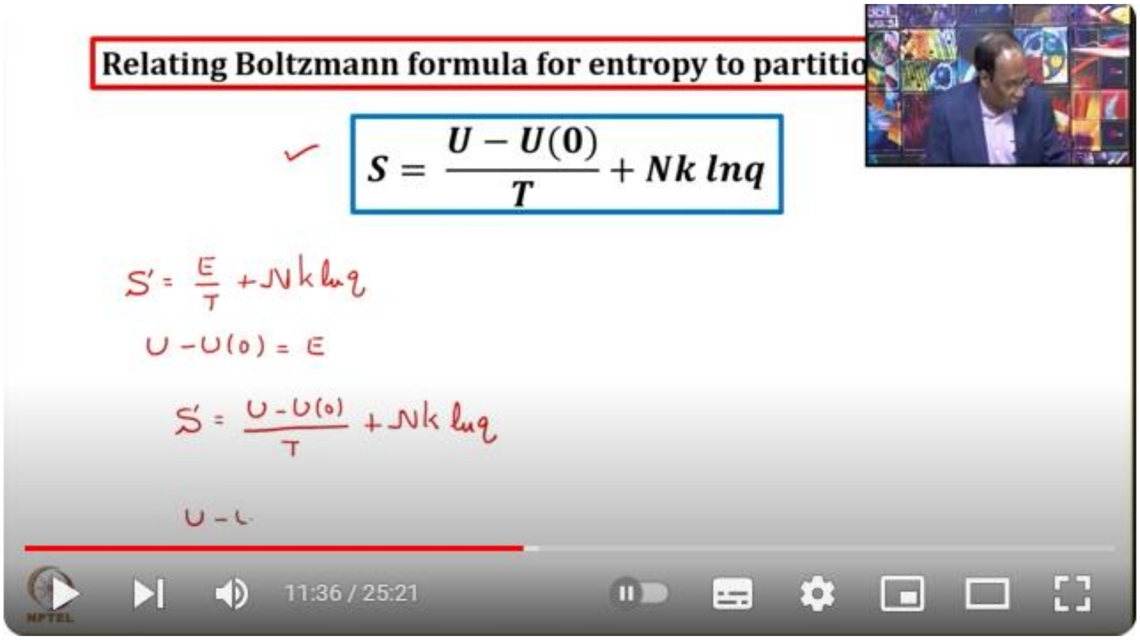

Relating Boltzmann formula for entropy to partitio

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

$$S' = \frac{E}{T} + Nk\,lnq$$

$$U - U(0) = E$$

$$S' = \frac{U - U(0)}{T} + Nk\,lnq$$

$U - U$

What we derived was S is equal to E total energy by T plus n K log q and remember that U minus U(0) is the total energy. So, therefore, let us substitute S is equal to U minus U(0) by T plus n K log q. We have now come up with an expression which connects entropy with the molecular partition function.

We already have developed equation for U minus U (0). Remember that U minus U(0) was equal to minus n by q *δ* q *δ* β at constant volume or remember that we said that we can also write this as minus n *δ* log q *δ* β at constant volume. So, U minus U(0) will come from here in terms of molecular partition function which can be substituted over here and n K log q. So, this is the relationship of Boltzmann formula for entropy to partition function. So, we have discussed relationship between

S and W. Remember that if you want to connect S and W that is S is equal to K log W and if you want to connect S and W, you want to connect entropy with the molecular partition function, then the expression to be used is this one. Let us try to apply this formula and calculate the entropy of a collection of n independent harmonic oscillators and further evaluate it using vibrational data for iodine vapors at 25 degrees centigrade.

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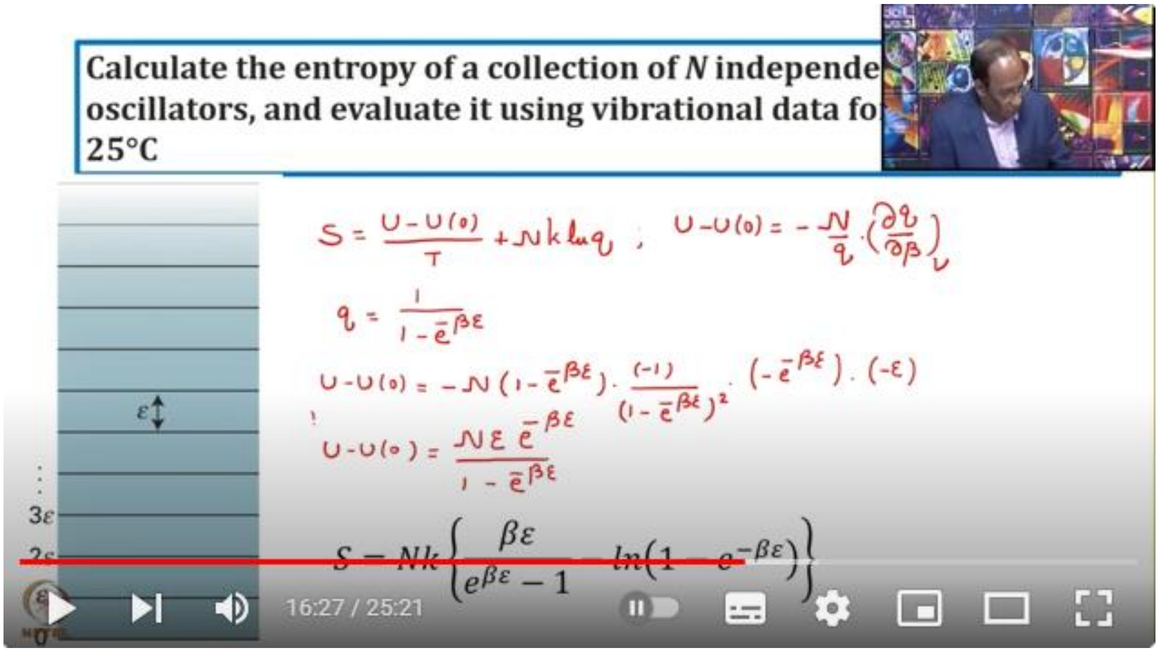

Calculate the entropy of a collection of *N* independe oscillators, and evaluate it using vibrational data fo 25°C

$$S = \frac{U - U(0)}{T} + Nk\ln q \;;\quad U - U(0) = -\frac{N}{q}\cdot\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$q = \frac{1}{1 - \bar{e}^{\beta\varepsilon}}$$

$$U - U(0) = -N\,(1 - \bar{e}^{\beta\varepsilon})\cdot\frac{(-1)}{(1 - \bar{e}^{\beta\varepsilon})^2}\cdot(-\bar{e}^{\beta\varepsilon})\cdot(-\varepsilon)$$

$$U - U(0) = \frac{N\varepsilon\,\bar{e}^{\beta\varepsilon}}{1 - \bar{e}^{\beta\varepsilon}}$$

$$S = Nk\left\{\frac{\beta\varepsilon}{e^{\beta\varepsilon} - 1} - \ln\left(1 - e^{-\beta\varepsilon}\right)\right\}$$

So, here we are talking about n independent harmonic oscillators. Harmonic oscillators will follow the arrangement of energy levels in a uniform ladder manner. So, this is a uniform ladder of energy levels.

We need to make use of this and we have just derived the expression that S is equal to U minus U(0) by T plus n k log q. So, this is the expression for energy levels. What we need here is u minus u 0. What is u minus u 0 is equal to minus n by q δ q δ β at constant volume. So, therefore, what kind of information I require? I require an expression for partition function, which we have already discussed for a uniform ladder of energy levels.

The partition function for a uniform ladder of energy levels was 1 over 1 minus exponential minus β u that we have derived earlier. Therefore, U minus U(0) is going to be minus n divided by q, which is 1 minus exponential minus β e into δ q by δ β at constant volume. So, we need to take a derivative of this. This is going to be minus 1 over 1 minus exponential minus β e whole square into minus exponential minus β e and into I have minus e. So, this is the expression for partition function.

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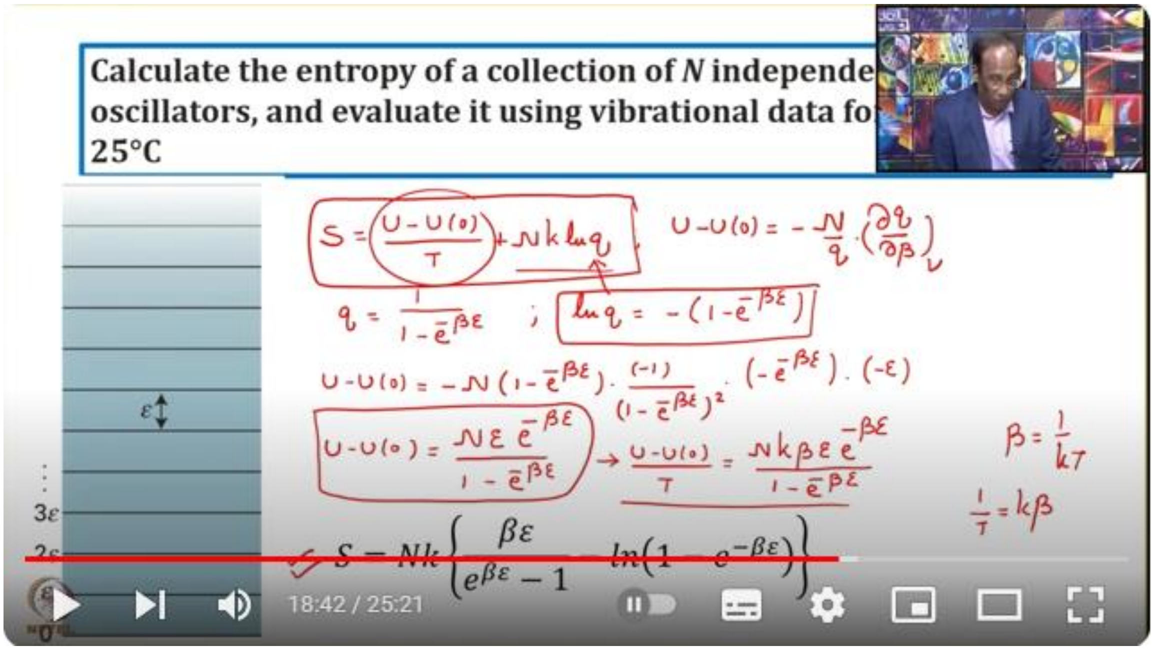

Calculate the entropy of a collection of N independe oscillators, and evaluate it using vibrational data fo 25°C

$$\boxed{S = \frac{U-U(0)}{T} + Nk\ln q} \qquad U-U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$q = \frac{1}{1-e^{-\beta\varepsilon}} \quad ; \quad \boxed{\ln q = -(1-e^{-\beta\varepsilon})}$$

$$U-U(0) = -N(1-e^{-\beta\varepsilon})\cdot\frac{(-1)}{(1-e^{-\beta\varepsilon})^2}\cdot(-e^{-\beta\varepsilon})\cdot(-\varepsilon)$$

$$\boxed{U-U(0) = \frac{N\varepsilon e^{-\beta\varepsilon}}{1-e^{-\beta\varepsilon}}} \rightarrow \frac{U-U(0)}{T} = \frac{Nk\beta\varepsilon e^{-\beta\varepsilon}}{1-e^{-\beta\varepsilon}} \qquad \beta = \frac{1}{kT} \qquad \frac{1}{T} = k\beta$$

$$S = Nk\left\{\frac{\beta\varepsilon}{e^{\beta\varepsilon}-1} - \ln(1-e^{-\beta\varepsilon})\right\}$$

Right? Minus n by q into δ q by δ β at constant volume. So, what I have now u minus u 0 is equal to 1 negative second third fourth. Fine. So, I have n from here, I have e from here, exponential minus β e and I have 1 minus exponential minus β e. From here, this is the expression for U minus U(0). U minus U (0) by t that is what we are interested is equal to n. What is 1 by t? Because 1 by t is equal to n minus U (0) by β is equal to 1 over k t. So, you use 1 over t is equal to k times β. So, 1 over t I will use as k times β k times β. I have e, I have exponential minus β e and then I have 1 minus exponential minus β e.

Okay? And then the second term is n k log q. Log q you can write from here, if q is one of the two terms, then you can write 1 over 1 minus exponential minus β e, then log q is going to be minus 1 minus exponential minus β e. So, once you have this, this log q can be substituted here and U minus U(0) by t, we already have n k β e exponential minus β e over 1 minus exponential minus β e. Substitute in this overall equation and you will get this result. Here, in order to get this result from this, I multiply a numerator and denominator by exponential β e.

So, therefore, the transformed result is going to be s is equal to n k β e over exponential minus β e. So, this is going to be n k log q. So, this is going to be n exponential β e minus 1 minus log 1 minus exponential β e. So, therefore, you can essentially here express entropy as a function of temperature from the knowledge of the energy separation for the harmonic oscillators. This is the expression which connects the entropy of a collection of n independent harmonic oscillators with temperature. The question is for iodine vapors. So, we need the data for iodine. We have derived this expression s is equal to n k β e over exponential β e minus 1 minus log into exponential 1 minus exponential β e and the system under consideration is uniform ladder of energy levels. The separation between simultaneous energy states or energy levels is e. The data given now for iodine is β e is 1.036 and molar entropy, once you substitute this number over here, the molar entropy comes out to be 8.

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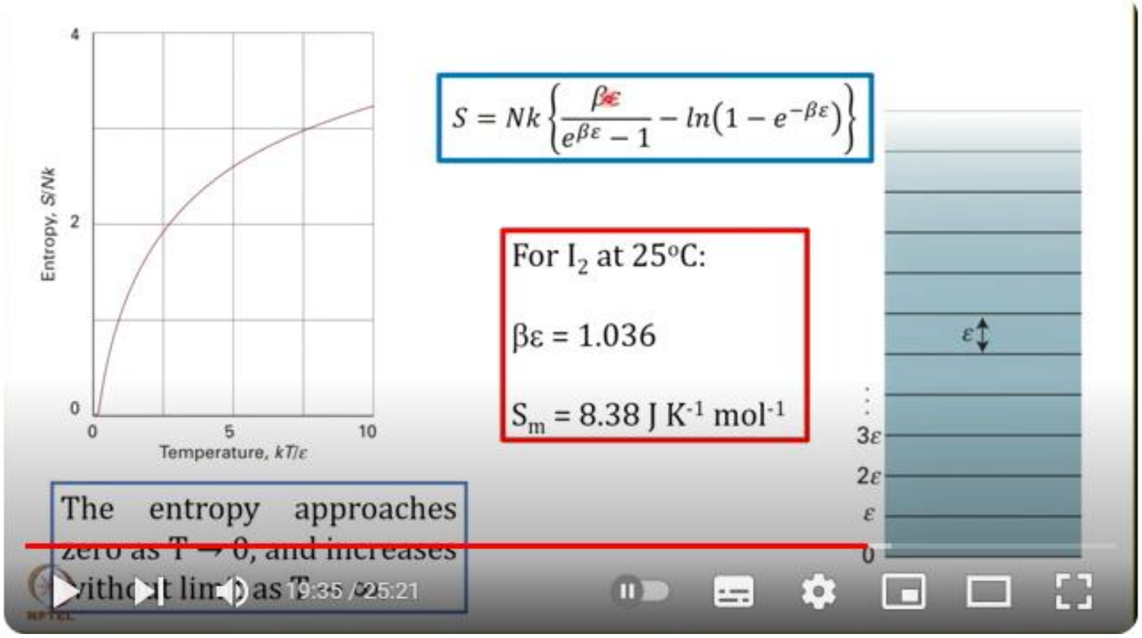

$$S = Nk\left\{\frac{\beta\varepsilon}{e^{\beta\varepsilon}-1} - ln\left(1-e^{-\beta\varepsilon}\right)\right\}$$

For I_2 at 25°C:

$\beta\varepsilon = 1.036$

$S_m = 8.38\ J\ K^{-1}\ mol^{-1}$

The entropy approaches zero as T → 0, and increases without limit as T

38 joules per kelvin per mole. This is at 25 degree centigrade, but the expression, this expression permits you to connect the entropy with the temperature here. And let us take a look at now the plot over here. The plot is entropy S by Nk. You can take Nk to the other side and plot s by Nk versus k T by e.

This is one way of plotting. Essentially you are plotting entropy versus temperature in some other form and from the plot you see here when temperature approaches 0, the entropy also approaches 0 and as the temperature increases, the entropy also increases in a manner which is without limit. So, this particular example is exclusively for harmonic oscillator. That is for a system which has a uniform ladder of energy levels and this expression allows us to interpret or discuss entropy as a function of temperature. Suppose if you have to deal with different systems where it is not a uniform ladder of energy levels and then you have to express entropy as a function of temperature, how will you do that? Let us have a discussion on that. S is equal to U minus U (0) by T plus n k plus Nk plus Nk plus n k plus n k.

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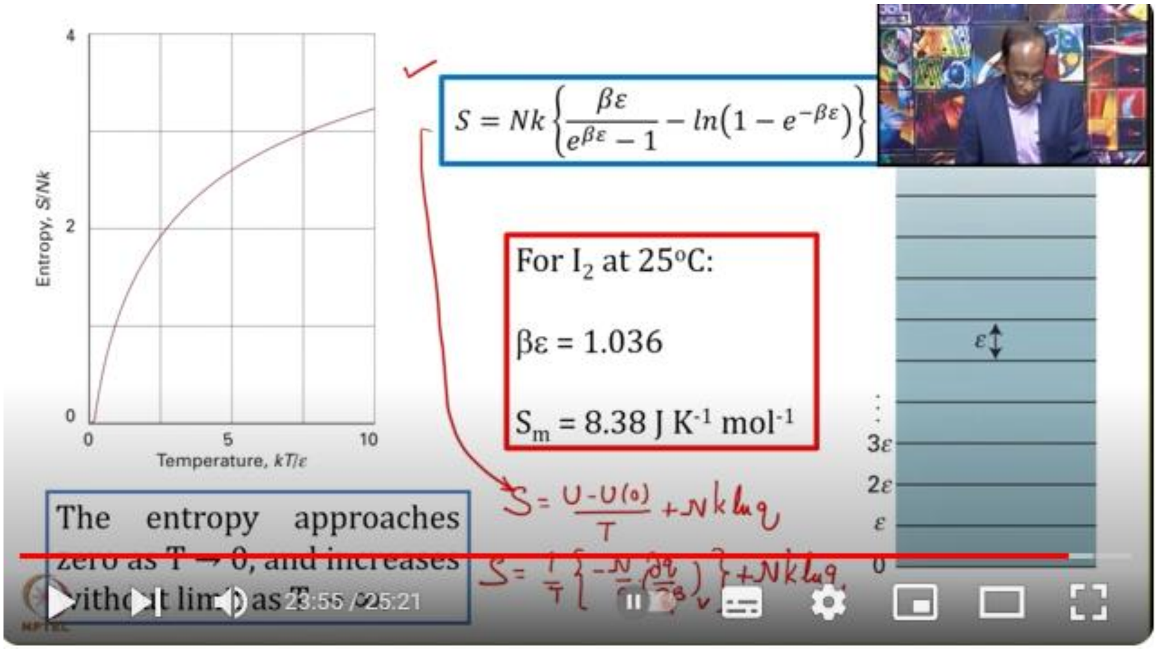

$$S = Nk\left\{\frac{\beta\varepsilon}{e^{\beta\varepsilon}-1} - ln\left(1-e^{-\beta\varepsilon}\right)\right\}$$

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

$$S = \frac{1}{T}\left\{-\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V\right\} + Nk\ln q$$

The entropy approaches zero as T → 0, and increases without limit as T

So, this expression that we have obtained is actually obtained based upon this expression and in order to obtain this expression, we need to have information on U minus U (0) by T and U minus U (0) by T is also expressed in terms of partition function. Let me complete this expression. This will be 1 by T and U minus U 0 is what? Is minus n by q δ q δ β at constant volume plus n k log q. So, essentially what we need is the information on molecular partition function. As I just discussed in this example, here we dealt with uniform ladder of energy levels. You can come across systems where there is doubly degenerate ground state, non-degenerate first excited state, doubly degenerate second state, doubly degenerate second excited state, triply degenerate next excited state. You should be able to write an expression for the molecular partition function. Once you know the expression for molecular partition function, substitute over here and obtain an expression for the entropy. So, what we discussed in this example is that we have to have a system of two different types of system. One is called the system of two different types of entropy.

So, what we discussed in this lecture is that, in order to obtain entropy, you need either an information on W, weight of a configuration or you need information on molecular partition function. Once we have information on W and q, we can easily write an expression for the entropy of the system. We will solve more numerical problems and discuss more applications on entropy in the next lecture. Thank you very much. Thank you.