Fundamentals of Statistical Thermodynamics

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Lecture – 15

Solving numerical problems based on Internal energy and Entropy

Welcome back to the next lecture on Fundamentals of Statistical Thermodynamics. So far we have developed equations which connect internal energy with molecular partition function and entropy with molecular partition function. Both these thermodynamic quantities internal energy and entropy are very important in thermodynamics. Internal energy is the total energy of the system added up in all the forms and entropy is a measure of degree of disorder or ordered state of a system. Why both these thermodynamic quantities are important? Because work or heat which both are equivalent form of energy when these are done on the system or these are done by the system these affect the internal energy. Work is done at the cost of internal energy.

Similarly entropy, if there is a change in entropy that can be connected with the creation of more order or more disorder. Going back to the second law of thermodynamics where we discussed that the change in entropy of an isolated system is positive for a spontaneous process. When I said I meant in change in entropy of the system plus change in entropy of the surroundings has to be positive if the process is to be spontaneous. Therefore, connecting internal energy with molecular partition function and entropy with molecular partition function is very important and it tells us how to determine these values by using spectroscopy.

Today we will use the derived equations to further discuss their applications. Let us take up the first example. In one of the previous lectures, we talked about heat capacity. So again revisiting heat capacity is a very important thermodynamic quantity because it connects one thermodynamic signature or one thermodynamic quantity at one temperature to the same thermodynamic quantity at another temperature. So therefore it is a connector for the thermodynamic quantities at different temperatures.

Not only that a literal definition of heat capacity is the amount of heat required to change the temperature of a system by one degree, one kelvin. That means it also directly talks about the strength of the system. If we impose constant volume constraints then the definition that we need to use is C_v is equal to δ U by δ t at constant volume. And in the previous, one of the previous lectures we have shown that u is equal to U (0) plus 3 N by

2 β. We also then derived this expression in terms of the Boltzmann constant, temperature, etcetera, and then we equated it equal to 3 by 2 nRT.

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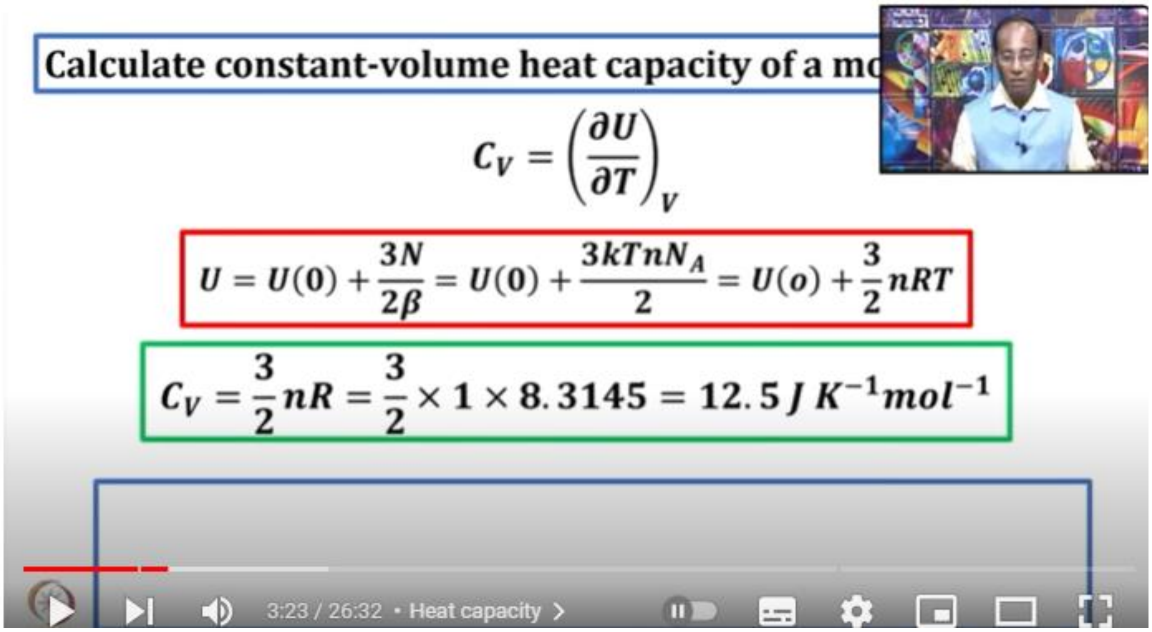

Calculate constant-volume heat capacity of a mo

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$U = U(0) + \frac{3N}{2\beta} = U(0) + \frac{3kTnN_A}{2} = U(o) + \frac{3}{2}nRT$$

$$C_V = \frac{3}{2}nR = \frac{3}{2} \times 1 \times 8.3145 = 12.5\, J\, K^{-1} mol^{-1}$$

This is for the translational motion of a particle of a molecule or of a molecule. I am talking about a monatomic type of gas in three dimensions. Substituting the numbers we got C_v equal to 12.5 joules per kelvin per mole. Let us highlight some of the comments. This value agrees almost exactly with the experimental data on monatomic gases at normal pressures. This is theoretical prediction. Second is experimental data and we have earlier talked about how to determine heat capacity experimentally. We need calorie meters. Under constant-volume conditions, bomb calorie meter.

Under constant pressure conditions, the other type of calorie meters which can work under constant pressure conditions. Second point that we need to be careful in this case about is that the value that we got 12.5 joules per kelvin per mole, it applies only to monatomic gas, monatomic perfect gas. And for more complex molecules, means for diatomic molecule, for triatomic molecules, there are other modes of motion which we need to consider. electronic, only translational degree of freedom is there. Electronic can also be there, but that can be discussed later. But when you go to diatomic and we go to triatomic and more complex molecules, then not only translational degree of freedom is there, there is rotational degree of freedom, there is vibrational degree of freedom in addition to electronic contributions. So, this is a very simple example. Now, let us go to some other type of questions. The question is to show that heat capacity of N two level systems, that is C_v is given by the following expression.

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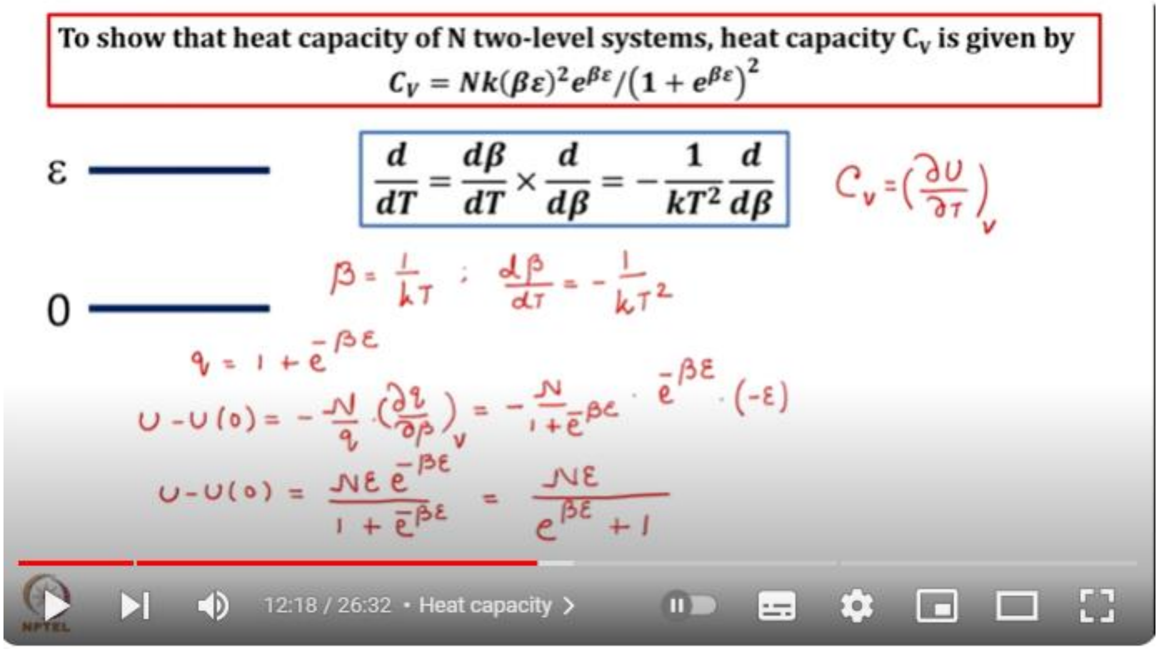

To show that heat capacity of N two-level systems, heat capacity C_V is given by

$$C_V = Nk(\beta\varepsilon)^2 e^{\beta\varepsilon}/\left(1+e^{\beta\varepsilon}\right)^2$$

$$\boxed{\frac{d}{dT} = \frac{d\beta}{dT}\times\frac{d}{d\beta} = -\frac{1}{kT^2}\frac{d}{d\beta}}$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$\beta = \frac{1}{kT} \; ; \; \frac{d\beta}{dT} = -\frac{1}{kT^2}$$

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

$$U - U(0) = -\frac{N}{q}\cdot\left(\frac{\partial q}{\partial \beta}\right)_v = -\frac{N}{1+e^{-\beta\varepsilon}}\cdot e^{-\beta\varepsilon}\cdot(-\varepsilon)$$

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

Cᵥ is equal to Nk into βE square exponential β Edivided by 1 plus exponential βEsquare and we know β is equal to 1 by kT. So, that means the expression that we are going to derive can allow us to calculate the value of C_v as a function of temperature and from the knowledge of energy separation. The given system is a two-level system and let us say separation between the ground state and the upper or the excited state is E. Alright. C_v basically by definition C_v is equal to δUδT at constant volume.

Now, either we can differentiate with respect to temperature and the result can also be expressed in terms of β. β and temperature anyway are connected to each other and sometimes instead of differentiating with respect to temperature, it becomes easier to differentiate with respect to β. So, you see d by dT, I can write d by dT as d β by dT into d by d β. Really that is allowed and since β is equal to 1 over kT, therefore d β over dT is going to be minus 1 over kT square. Therefore in place of d β by dT, I can write minus 1 over kT square and then I can write differentiation with respect to β. Why this kind of transformations? Why this kind of derivatives? Because sometimes it becomes easier if we work in terms of d by dβ. You can work in terms of d by dT and then convert into β. Choice is yours. But as I said that sometimes if we choose an appropriate derivative, it is easier to get results. Now let us come back to the problem that we need to solve. We have these two levels, ground state and upper state. The first step will be to write partition function which will be 1 plus exponential minus β. For ground state 1, for upper state the contribution is exponential minus β. C_v is a derivative of internal energy. So therefore, first of all let us talk about internal energy. U minus U (0) is equal to minus N by q δ q δ β at constant volume. q is 1 plus exponential minus β E. So therefore, let us now work on this. Minus N by q minus N by q . q is 1 plus exponential minus βE and into derivative of q with respect to β which is exponential minus β E and into it is going to be minus E.

So what I have now is U minus U (0) is equal to minus minus is plus. So it is nE exponential minus β E divided by 1 plus exponential minus β E.

I can further simplify it. I can multiply numerator and denominator with exponential plus βE. Exponential plus β E. Why? Because if I multiply by exponential plus β E, this upper term becomes 1. So I have N E into 1 that I am not writing divided by exponential βE plus 1. Just to make the things little more simpler. We have now the expression for internal energy and if we take its derivative with respect to temperature or with respect to β, then we will get the heat capacity. What we have is now U minus U (0) is equal to nE over exponential βE plus 1.

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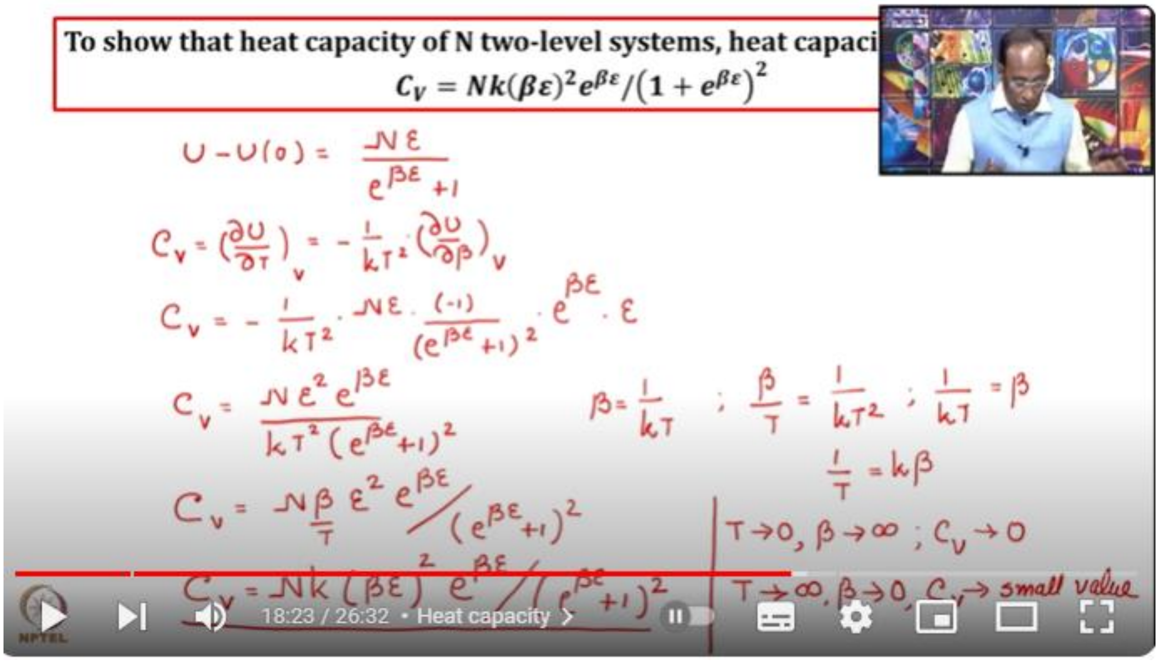

To show that heat capacity of N two-level systems, heat capaci

$$C_V = Nk(\beta\varepsilon)^2 e^{\beta\varepsilon}/\left(1+e^{\beta\varepsilon}\right)^2$$

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

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = -\frac{1}{kT^2}\cdot\left(\frac{\partial U}{\partial \beta}\right)_v$$

$$C_v = -\frac{1}{kT^2}\cdot N\varepsilon\cdot\frac{(-1)}{(e^{\beta\varepsilon}+1)^2}\cdot e^{\beta\varepsilon}\cdot\varepsilon$$

$$C_v = \frac{N\varepsilon^2 e^{\beta\varepsilon}}{kT^2(e^{\beta\varepsilon}+1)^2}$$

$$\beta = \frac{1}{kT} \quad ; \quad \frac{\beta}{T} = \frac{1}{kT^2} \quad ; \quad \frac{1}{kT} = \beta$$

$$\frac{1}{T} = k\beta$$

$$C_v = N\frac{\beta}{T}\varepsilon^2 e^{\beta\varepsilon}/(e^{\beta\varepsilon}+1)^2$$

$$C_v = Nk(\beta\varepsilon)^2 e^{\beta\varepsilon}/(e^{\beta\varepsilon}+1)^2$$

$T \to 0, \beta \to \infty \; ; \; C_v \to 0$

$T \to \infty, \beta \to 0, C_v \to$ small value

That is what we have. C_v is equal to δU δT at constant volume and we just showed that it is equal to minus 1 over K T square into I can write δ U δ β at constant volume. We just showed that. Now let us act upon this. So what we have? C_v is equal to minus 1 over K T sq uare into let us take the derivative of internal energy with respect to β. N E is anyway there constant into minus 1 over exponential β E plus 1 square into exponential β E into E.

Let's further simplify it. So C_v is equal to what do I have? Minus minus becomes plus. So I have N then I have E square I have exponential β E over K T square into exponential βE plus 1 whole square. I have combined the terms and I have N into E square into exponential β E divided by KT square exponential β E plus 1. We can now further simplify it by noting that β is equal to 1 over K T. Now I can write this as β over T is equal to 1 over KT square.

So I want to simplify my result. I have C_v is equal to N instead of 1 by KT square let me write β by T into E square exponential β E divided by exponential β plus 1 square. Now remember that I can write another term from here 1 over K T 1 over K T is equal to β which means 1 over T is equal to K tmes β. I can use it over here 1 over T is equal to K times β that means what I have now is once I substitute over here C_v is equal to 1 over T is K times β so I have N K and another β term will come β E square let me combine all this β E square into exponential β E by exponential β E plus 1 square. So I have this result C_v is equal to Nk into β E whole square exponential β E divided by exponential β E plus 1 this is what we were asked to show.

Remember that β is equal to 1 over K T. Now we can briefly talk about effect of temperature on this result. We will use this expression that we derived and let us see what happens when temperature approaches 0. When the temperature approaches 0 then β is equal to 1 over K T that means β will approach a value of infinity and you see you have infinity in the denominator also. So C_v will approach a value of 0. You have infinity in the denominator and when T approaches infinity then β is 1 over K T that means β approaches a value of 0. Then you see here you have 0 then also that means C V will approach a very small value and if you work out actually take a maximum also it will show a maxima too. So in general what I want to say here is that depending upon the system given to you. For example, here we were talking about N_2 level systems and we discussed that each level is a non-degenerate and therefore we wrote an expression for the molecular partition function for that and then we developed further equations. This is showing that the heat capacity of N_2 level systems is given by some kind of expression which permits us to calculate C_v as a function of temperature from the knowledge of energy levels or energy separation.

hope this derivation is clear. Now let us go to another type of question. We have a similar system now. N_2 level systems evaluate the molar entropy of N_2 level systems and then plot the resulting expression.

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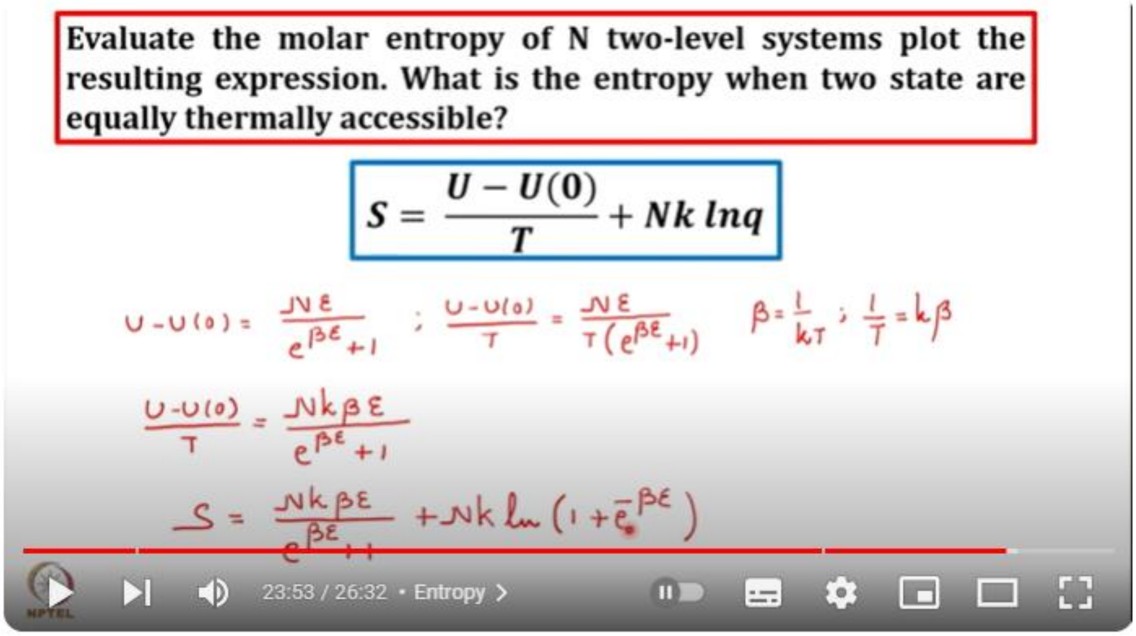

Evaluate the molar entropy of N two-level systems plot the resulting expression. What is the entropy when two state are equally thermally accessible?

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

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

$$\frac{U-U(0)}{T} = \frac{Nk\beta\varepsilon}{e^{\beta\varepsilon}+1}$$

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

What is the entropy when two states are equally thermally accessible? In the previous question we talked about internal energy and then we talked about connection of internal energy with partition function and eventually an expression for the heat capacity. Now we will be talking about entropy and entropy is connected to molecular partition function through this equation.

S is equal to U minus U (0) by T plus Nk log q and remember that U minus U (0) is also connected to the molecular partition function. U minus U (0) for the same system which is given to us N $_2$ level systems, we have just discussed that U minus U (0) is equal to, we derive the expression which is N times E over exponential β E plus 1. This is the expression that we derived in the previous lecture. I can take you back to the previous lecture and this is where look at this expression that U minus U (0) we have derived this expression is equal to N times E divided by exponential β E plus 1. Let us make use of this now. So that means U minus U (0) by T will be equal to what? Which will be nE over T times exponential β E plus 1 and since we decided that instead of T let us talk in terms of β. That means β is equal to 1 over k T or we use 1 over T is equal to k times β. We will use that that means U minus U (0) by T is equal to 1 over T is k β. So Nkβ I am writing instead of 1 over T E over exponential βE plus 1. This is U minus U (0) by T. Now we can write the expression for entropy. S is equal to U minus U (0) by T is N k β E divided by exponential β E plus 1 plus Nk log q plus Nk log q q is what? It is a two-level system 1 plus exponential minus β E.

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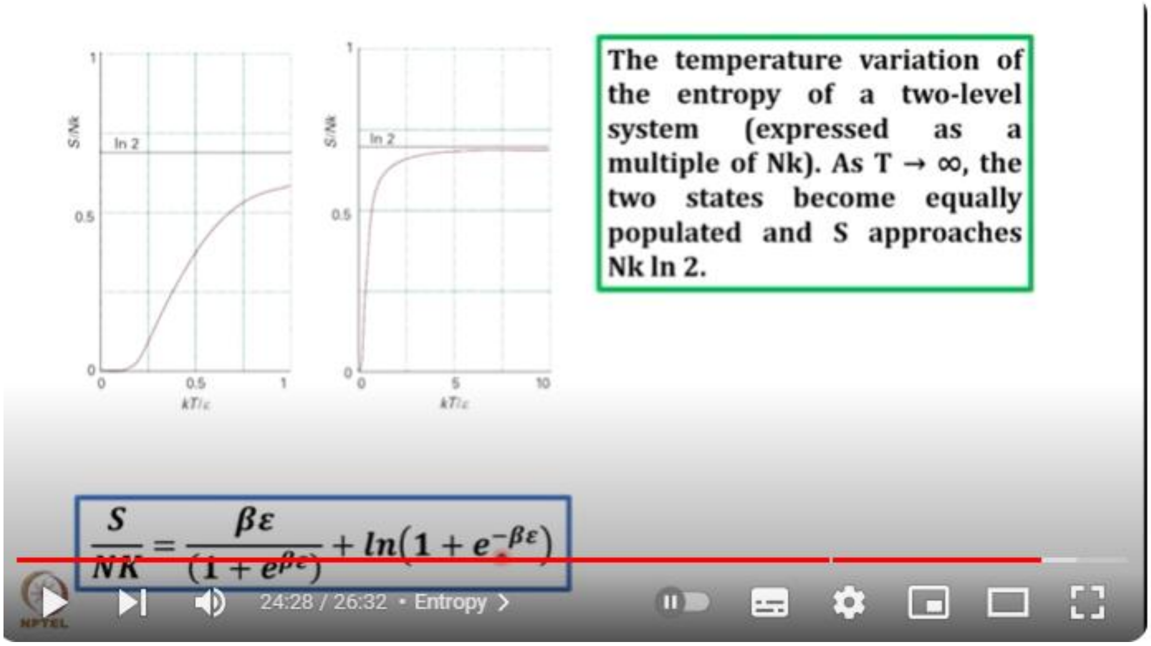

The temperature variation of the entropy of a two-level system (expressed as a multiple of Nk). As T → ∞, the two states become equally populated and S approaches Nk ln 2.

$$\frac{S}{NK} = \frac{\beta\varepsilon}{(1+e^{\beta\varepsilon})} + ln(1+e^{-\beta\varepsilon})$$

Check carefully what you have is S is equal to N k into β E divided by exponential β E plus 1 that is U minus U (0) by T plus Nk log q. Nk is common. So therefore I can take it on the left-hand side and then express in terms of S by Nk. Once we do that what we have is the following expression. S by Nk is equal to β E over 1 plus exponential β E plus log 1 plus exponential minus β E. That is what I was saying that this Nk and Nk is common and you can take it on the other side and eventually the expression that you get is S upon Nk is equal to β E over 1 plus exponential β E plus log into 1 plus exponential minus β E.

We have now entropy as a function of temperature. It is not a linear or very simple function. You see β 1 over T is appearing here, 1 over T is appearing here, 1 over T is appearing here. So, therefore we can easily talk about in the extreme limits that is when temperature approaches 0 or when temperature approaches infinity. But remember that the expression that we have got here is for N_2 level systems, a ground state and an excited state which is separated by energy E. We have now connected the entropy of such a system with temperature energy separation by this expression. We need to further discuss the variation of entropy with temperature in this case in the limits of T approaching 0 and T approaching infinity, but that we will do in the next lecture. Thank you very much.