Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

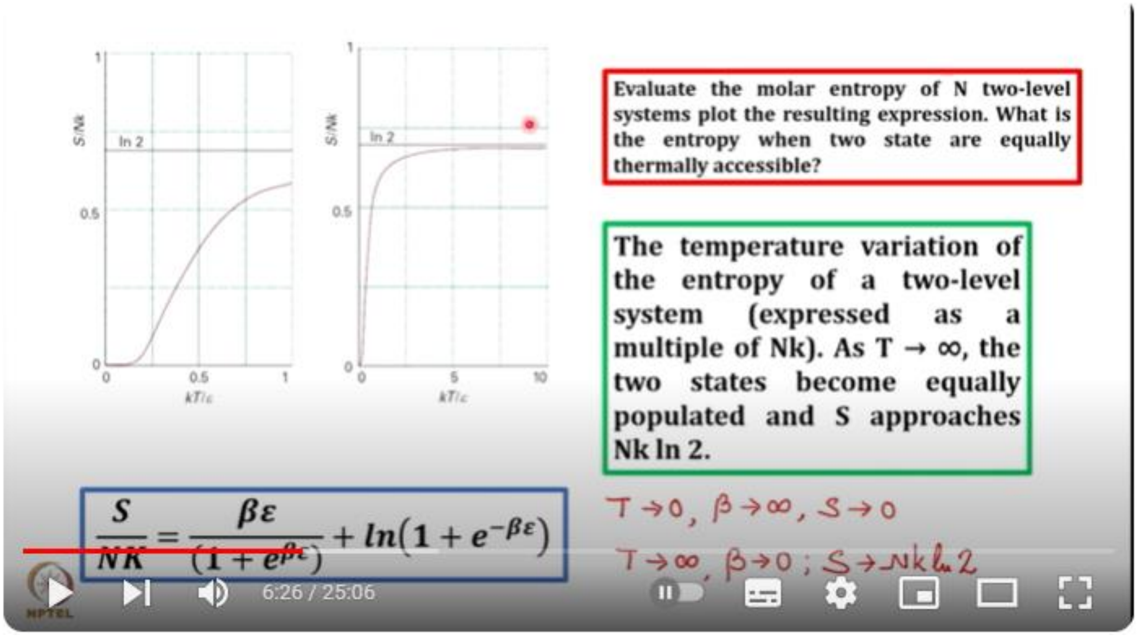
Indian Institute of Technology, Bombay

Lecture – 16

Solving numerical problems based on Internal energy and Entropy

Let us continue our discussion on solving numerical problems based on internal energy and entropy. Internal energy and entropy are directly connected to each other. Go back to concepts of chemical thermodynamics where you remember that dS which is equal to dq by T allows you to connect under constant volume conditions dU is equal to TdS. So, therefore, internal energy and entropy can be directly connected. In the previous tutorial session, we talked about evaluating the molar entropy of N two-level systems and we were also asked to plot the resulting expression.

See Slide time: 6:26



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

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.

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

$T \to 0,\ \beta \to \infty,\ S \to 0$

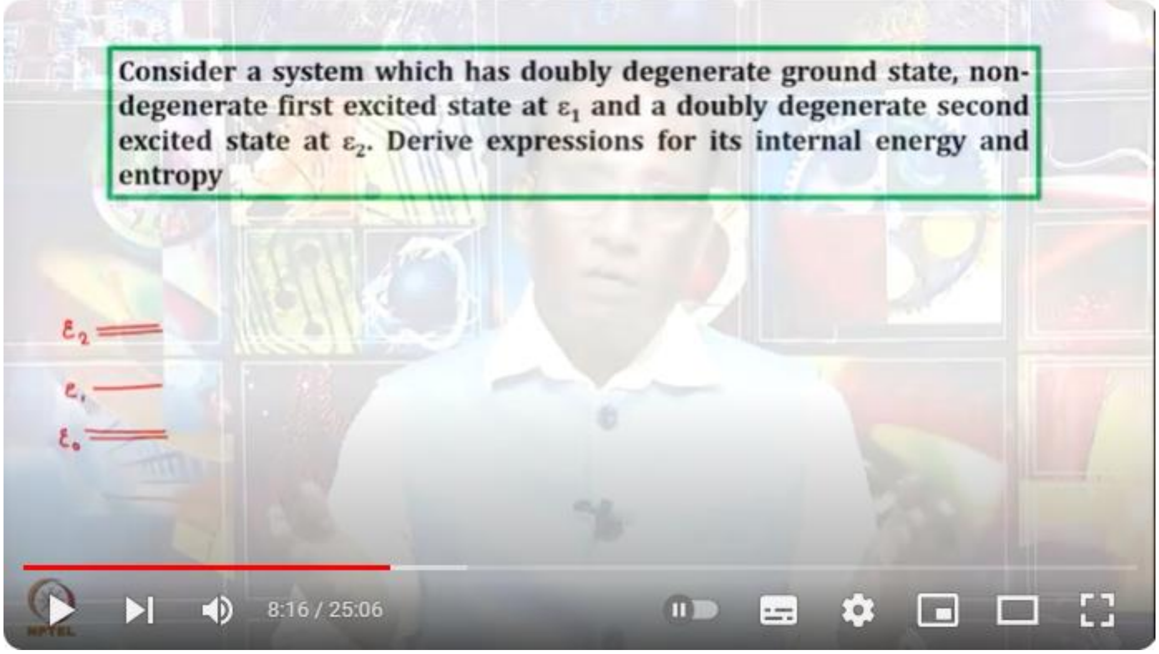
$T \to \infty,\ \beta \to 0;\ S \to Nk\ln 2$

First let us discuss that. We have already shown the dependence of entropy upon temperature or β through this expression S by NK is equal to β E divided by one plus exponential β E then plus log one plus exponential minus β E. And when you plot this, look into the upper figures. It is plotted as S by NK versus kT by epsilon and you see when the temperature is increasing, the value is starting from zero and eventually rising towards a final value of log two. So this is how the entropy dependence upon temperature can be expressed.

So definitely we can exactly find out the value of entropy when temperature is approaching zero and the second is when temperature is approaching infinity. Now I want you to take a look at the statement of the question that is given to us. Evaluate the molar entropy of N two level systems and plot the resulting expression, we have plotted. What is the entropy when two states are equally thermally accessible? So if we are considering only two states, two levels, then at what temperature the two-states are equally thermally accessible? We have already discussed that when temperature approaches infinity. Remember that when we talked about the fractional population of a system which has only two-states as the temperature approaches infinity, both the states are equally thermally accessible.

We also derived a general conclusion at that time that whatever is the state under consideration, when temperature approaches infinity, all the states are equally thermally accessible. But let us talk about what happens when temperature approaches zero. When temperature approaches zero, then β over k T, β is equal to one over k T, then β approaches infinity, but here there is a denominator infinity also and here minus infinity that means this one over exponential infinity, this will become zero. So log one, log one is also zero. This is zero because there is infinity in the denominator that means S approaches a value of zero. That is what you observe over here. When temperature approaches zero, S approaches a value of zero. Now the second condition, when the two states are equally thermally accessible that means we are talking about a temperature which is very very high approaching infinity. Let us work on that. When temperature approaches infinity, then β which is 1 over k T approaches a value of zero.
So this factor, the first one, this becomes zero and this exponential zero, this becomes one. So log one plus one, then you have two. So when β approaches zero, this first term is zero and then log two. S by n k is equal to log two that means S approaches a value of n k log two. So therefore, such an expression, it allows us to express entropy as a function of temperature. We can talk very easily the situations when temperature approaches zero and the temperature approaches a very high value. At the intermediate temperatures, one can use this expression and calculate the value of entropy. Now let us talk about another case. Consider a system which has doubly degenerate ground state, non-degenerate first excited state at E_1 and a doubly degenerate second excited state at E_2. Derive expressions for its internal energy and entropy.

See Slide time: 8:16

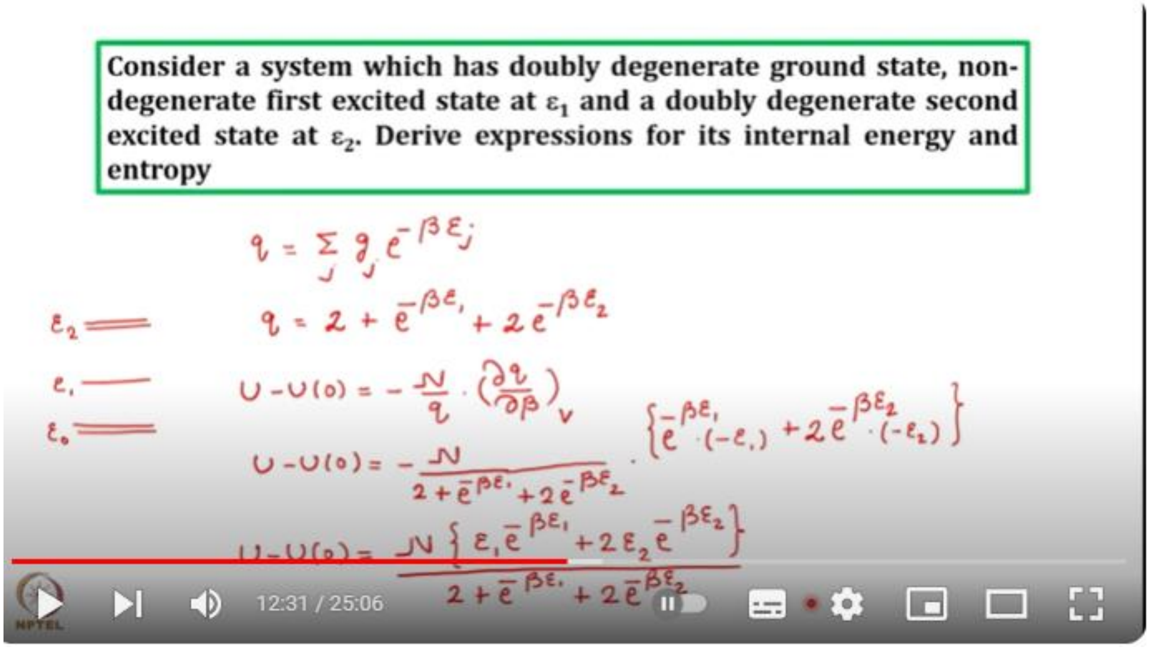


Consider a system which has doubly degenerate ground state, non-degenerate first excited state at ε_1 and a doubly degenerate second excited state at ε_2. Derive expressions for its internal energy and entropy

Let us try to understand this problem. Consider a system which has a doubly degenerate ground state. Let us write that. There is a doubly degenerate ground state, a non-degenerate first excited state. Let us say this is a non-degenerate first excited state and the energy here is E_1 and a doubly degenerate second excited state. Let us say there is a second excited state which is doubly degenerate and this is at E2. This is E0, E0 is equal to zero. Derive expressions for its internal energy and entropy. Whether you want to derive expression for internal energy or you want to derive expression for entropy, we first need an expression for its partition function. Let us write down an expression for its partition function.

Diction function is summation j g_j exponential minus β Ej. Apply to this system q is equal to g_0. g_0 degeneracy of the ground state is 2 plus g1 degeneracy of the first excited state is 1 into exponential minus β E_1. And then we have degeneracy of the second excited state which is 2 exponential minus β E_2. This is the expression that I have for the molecular partition function. Once I have this expression for the partition function, now I can write an expression for internal energy. Remember, u minus u0, this is the internal energy is equal to minus n by q δ q δ β at constant volume.

See slide time: 12:31



Consider a system which has doubly degenerate ground state, non-degenerate first excited state at ε_1 and a doubly degenerate second excited state at ε_2. Derive expressions for its internal energy and entropy

$$q = \sum_j g_j e^{-\beta\varepsilon_j}$$

$$q = 2 + e^{-\beta\varepsilon_1} + 2e^{-\beta\varepsilon_2}$$

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

$$U - U(0) = -\frac{N}{2 + e^{-\beta\varepsilon_1} + 2e^{-\beta\varepsilon_2}}\cdot\left\{e^{-\beta\varepsilon_1}\cdot(-\varepsilon_1) + 2e^{-\beta\varepsilon_2}\cdot(-\varepsilon_2)\right\}$$

$$U - U(0) = \frac{N\left\{\varepsilon_1 e^{-\beta\varepsilon_1} + 2\varepsilon_2 e^{-\beta\varepsilon_2}\right\}}{2 + e^{-\beta\varepsilon_1} + 2e^{-\beta\varepsilon_2}}$$

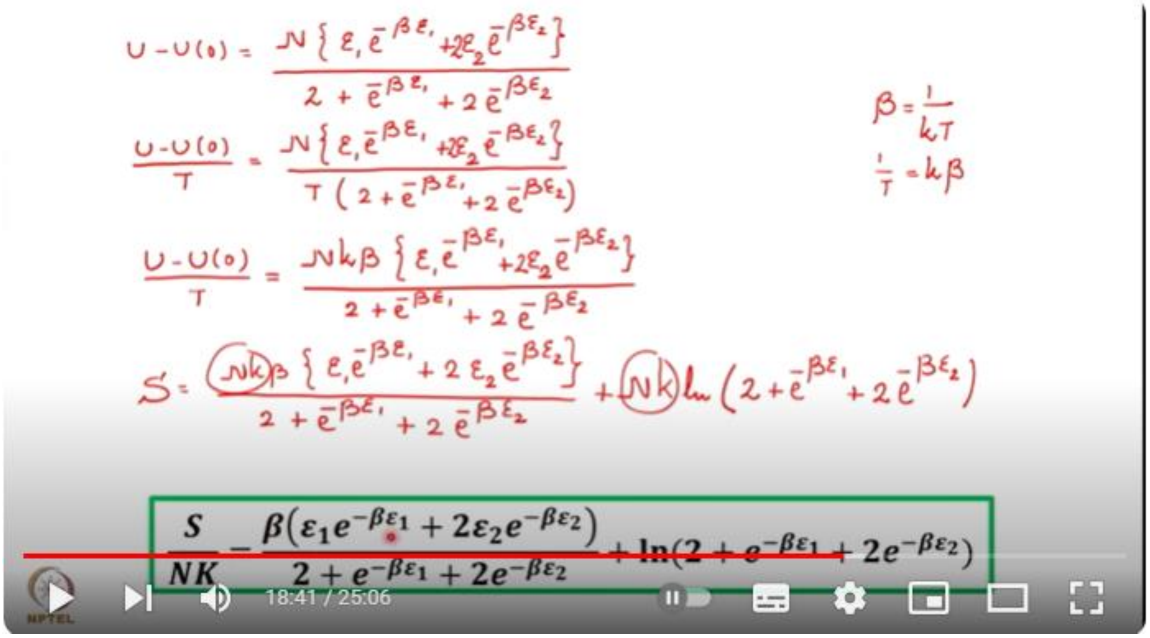
We already have an expression for q. So therefore, it becomes easier for us now to write an expression for internal energy. u minus u0 is equal to minus n by q. q is 2 plus exponential minus β E_1 plus 2 exponential minus β E_2 into derivative of this with respect to β. This is going to be exponential minus β E_1 into minus E_1 plus 2 times exponential minus β E_2 into minus E_2. So what I have now is u minus u0 is equal to, I can consume all the negatives with this negative and turn it into positive. So what I have is n and then I have E1 exponential minus β E_1 plus 2 E_2 exponential minus βE_2. In the denominator, I have 2 plus exponential minus β E_1 plus 2 exponential minus βE_2.

This is the expression for internal energy. You can calculate internal energy for this system as a function of temperature. Carefully note that in the previous example when we considered only two-level systems q was different. Here we are taking n systems where the ground state is doubly degenerate, the first excited state is non-degenerate, second excited state is doubly degenerate, the q is getting modified and as a result of this modification, your expressions for the internal energy are also getting modified. Therefore, the temperature dependence of internal energy on temperature is going to be this complex function.

You can always talk about temperature approaching 0 and temperature approaching infinity as extreme cases. Now that we have the expression for internal energy, you can also now derive an expression for heat capacity at constant volume from this expression because you remember that Cv is δ u by δ t at constant volume or is equal to minus 1 over kT square into δ U by δ β at constant volume and you can have an expression of heat capacity as a function of β or as a function of temperature, which is also going to be relatively a complex function. But the question that we are supposed to solve is to derive expressions for internal energy and entropy. We have an expression for internal energy. Okay. What we derived just now is U minus U (0) is equal to what I had there was let us take a look back what we had. We had this n times E_1 exponential this term and over q. Let us take it to the next one. This is equal to n then we have E1 exponential minus β E1 plus E2 exponential minus β E2 and then in the denominator we had the molecular partition function 2 plus exponential minus β E1 plus 2 exponential minus β E2. This is U minus U(0). u minus u0 by T will be equal to n E1 exponential minus β E1 plus E2 exponential minus β E2 divided by T into 2 plus exponential minus β E1 plus 2 exponential minus β E2 and we can use the usual transformations that β is equal to 1 over kT that means 1 over T is equal to k times β. I can use that. So, what I have is now u minus u0 by T is equal to 1 over T I am writing k β. So, I have n I have k into β inside I have E1 exponential minus β E1 plus E2 exponential minus β E2 and here I have is 2 plus exponential minus β E1 plus 2 into exponential minus β E2. Keep a factor of 2 over here which we missed.

So, I have this. So, we have U minus U (0) by T. So, S is equal to U minus U (0) by T which is n k β inside I have E_1 exponential minus β E_1 plus 2 E_2 exponential minus β E2 divided by 2 plus exponential minus β E_1 plus 2 exponential minus 2 E_2 plus n k log q n k log q q was 2 plus exponential minus β E_1 plus 2 exponential minus β E_2.

See Slide time: 18:41



$$U-U(0)=\frac{N\{\varepsilon_1 e^{-\beta\varepsilon_1}+2\varepsilon_2 e^{-\beta\varepsilon_2}\}}{2+e^{-\beta\varepsilon_1}+2e^{-\beta\varepsilon_2}}$$

$$\beta=\frac{1}{kT}$$

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

$$\frac{U-U(0)}{T}=\frac{N\{\varepsilon_1 e^{-\beta\varepsilon_1}+2\varepsilon_2 e^{-\beta\varepsilon_2}\}}{T(2+e^{-\beta\varepsilon_1}+2e^{-\beta\varepsilon_2})}$$

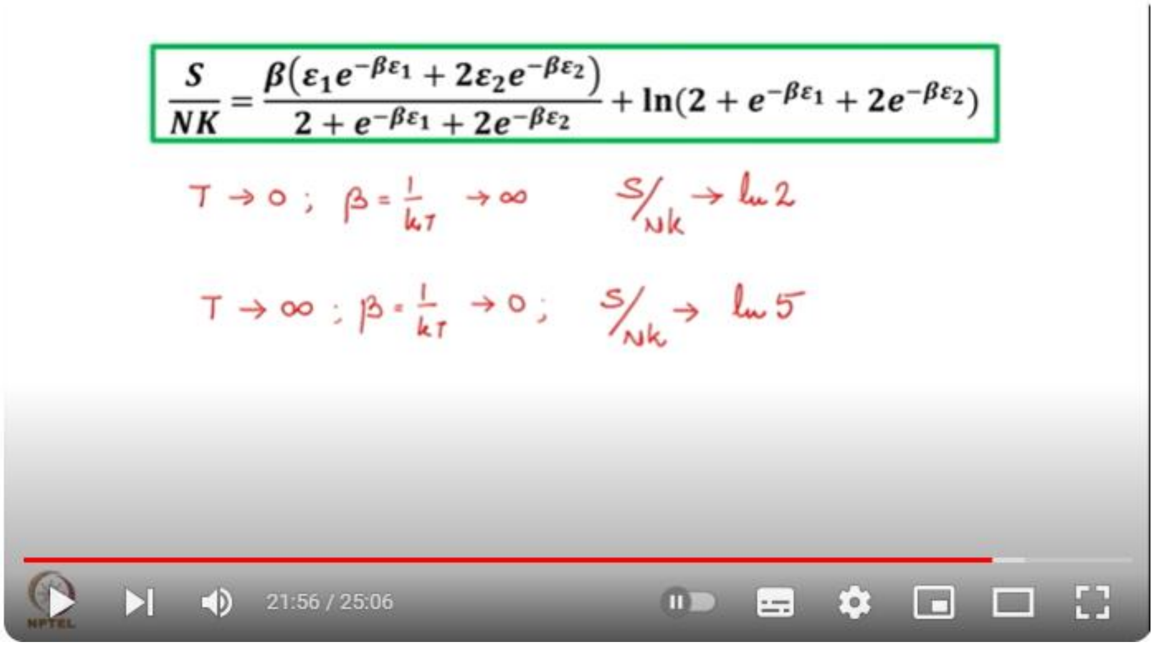
$$\frac{U-U(0)}{T}=\frac{Nk\beta\{\varepsilon_1 e^{-\beta\varepsilon_1}+2\varepsilon_2 e^{-\beta\varepsilon_2}\}}{2+e^{-\beta\varepsilon_1}+2e^{-\beta\varepsilon_2}}$$

$$S=\frac{\boxed{Nk}\beta\{\varepsilon_1 e^{-\beta\varepsilon_1}+2\varepsilon_2 e^{-\beta\varepsilon_2}\}}{2+e^{-\beta\varepsilon_1}+2e^{-\beta\varepsilon_2}}+\boxed{Nk}\ln(2+e^{-\beta\varepsilon_1}+2e^{-\beta\varepsilon_2})$$

$$\boxed{\frac{S}{NK}=\frac{\beta(\varepsilon_1 e^{-\beta\varepsilon_1}+2\varepsilon_2 e^{-\beta\varepsilon_2})}{2+e^{-\beta\varepsilon_1}+2e^{-\beta\varepsilon_2}}+\ln(2+e^{-\beta\varepsilon_1}+2e^{-\beta\varepsilon_2})}$$

NK is common therefore, the resulting expression is S by NK is equal to β into E1 exponential minus β E_1 plus $2E_2$ exponential minus β E_2 divided by the partition function that is 2 plus exponential minus β E_1 plus 2 into exponential minus β E_2 plus log 2 plus exponential minus β E_1 plus twice exponential minus β E_2. This was the expression to be derived. Look at the nature of the expression dependence of entropy on temperature. It is a complex function, but if you know the values of temperature, if you know the values of the first state energy state and the second excited energy state these numbers if you know then you can definitely calculate entropy at a given temperature. But remember that you can always calculate these values at extremes of temperature for the sake of simplicity. What I mean is let us discuss what happens when temperature approaches a value of 0. When the temperature approaches a value of 0 then β which is equal to 1 over k T when the temperature approaches 0 this will approach a value of infinity. So, therefore, what you have is here in the denominator you have infinity. So first term is 0 and the second term because it is infinity exponential minus infinity that means 1 over exponential infinity this becomes 0 this becomes 0. So therefore, what you have is S over NK is actually approaching a value of log 2. Now the second one is when temperature approaches a value of infinity then β is equal to 1 over k T it will approach a value of 0. That means what we have now we have this β is equal to 0. So that will set everything equal to $0N_o$ contribution from first term. But second term you will have 1 from here and 2 from here because exponential minus 0 or exponential 0 that is 1.

See Slide time: 21:56



$$\boxed{\frac{S}{NK} = \frac{\beta\left(\varepsilon_1 e^{-\beta\varepsilon_1} + 2\varepsilon_2 e^{-\beta\varepsilon_2}\right)}{2 + e^{-\beta\varepsilon_1} + 2e^{-\beta\varepsilon_2}} + \ln\left(2 + e^{-\beta\varepsilon_1} + 2e^{-\beta\varepsilon_2}\right)}$$

$$T \rightarrow 0\ ;\ \beta = \frac{1}{kT} \rightarrow \infty \qquad S/_{Nk} \rightarrow \ln 2$$

$$T \rightarrow \infty\ ;\ \beta = \frac{1}{kT} \rightarrow 0\ ; \qquad S/_{Nk} \rightarrow \ln 5$$

So that means what we have now S upon NK will approach a value of log 2 plus 1 3 3 plus 2 5 points to be noted here. The third law of thermodynamics says that every substance has a positive entropy which may become 0 at absolute 0 and it does become 0 for perfectly crystalline substances. But it did not say that all the substances have to have a value of entropy equal to 0. Here is one such case which you come across that when the temperature is approaching 0 your entropy is approaching a value of NK log 2 and when temperature is approaching infinity then S is approaching a limiting value of NK log 5.

So when there is some amount of entropy even when the temperature is approaching 0 that means even at 0 there is some sort of disorder. So at absolute 0 that some sort of disorder can come from configurational disorder and that configurational disorder can give rise to some value of entropy even at absolute 0. The concept of entropy at absolute 0 which is called residual entropy we will discuss at a later stage. In today's lecture what we have done is we have combined the connection of internal energy with molecular partition function and the connection of entropy with internal energy and molecular partition function. So this discussion allowed us to derive expressions for the variation of internal energy with temperature and variation of entropy with temperature. I hope that the numerical problems discussed in these two sessions have enabled you to appreciate the relationship of internal energy with molecular partition function and the relationship of entropy with molecular partition function in a more simpler and clearer manner. Thank you very much. Thank you.