Fundamentals of Statistical Thermodynamics

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Lecture – 13

The Statistical Entropy

Today, we are going to discuss another very important thermodynamic quantity that is entropy. Remember that, entropy is connected with spontaneity. All the processes occur in the direction which lead to overall increase in entropy. When I say overall increase in entropy, that means, I am talking about entropy change in the system, entropy change in the surroundings. This is about entropy change. And then you remember in the third law of thermodynamics, we also talked about the entropy of a substance.

We talked about entropy at absolute zero and then we also discussed the formal definition of the third law of thermodynamics that the entropy of each substance is positive, which may become zero at absolute zero and it does become zero at absolute zero for perfectly crystalline substances. Today, we are going to talk about statistical entropy. We are going to derive some formulae, connect statistical entropy or entropy with the weight of most probable configuration, and then eventually we will establish a relationship between entropy and molecular partition function. Let us get started with that.

Our first goal is going to be establishing a relationship between entropy and weight of a configuration. Now, how do we go about this derivation? Remember that the definition of change in entropy dS, remember from the discussion in chemical thermodynamics that dS, there we defined as dq_{rev} by T. Keep it in mind that dS is not just equal to dq by T, dS is equal to dq reversible by T that means, you have to connect the path reversibly. Now, one usually talks about either constant pressure conditions or constant volume conditions. Let us say, since we have been talking so far about constant volume conditions that means, at constant volume, I will say this is equal to dq volume is equal to du by T at constant volume that means, in order to connect change in entropy with partition function because remember that we have already derived a relationship between internal energy and molecular partition function. So, therefore, if I connect the change in entropy with internal energy, maybe I can find out some way of eventually connecting entropy with the partition function. So, if I am talking about the internal energy that means, I am also talking about the total energy because total energy and internal energy are connected with each other. Let us write such a relation, internal energy is equal to U (0) plus total energy.

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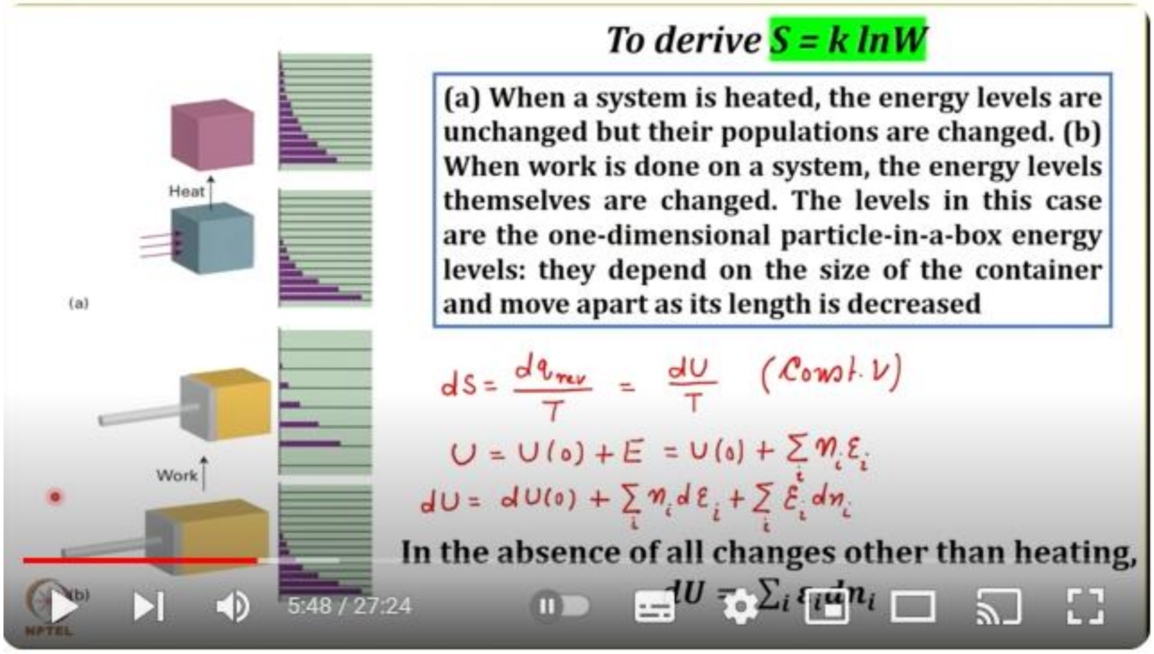

To derive S = k lnW

(a) When a system is heated, the energy levels are unchanged but their populations are changed. (b) When work is done on a system, the energy levels themselves are changed. The levels in this case are the one-dimensional particle-in-a-box energy levels: they depend on the size of the container and move apart as its length is decreased

$$dS = \frac{dq_{rev}}{T} = \frac{dU}{T} \quad (\text{Const. } V)$$

$$U = U(0) + E = U(0) + \sum_i n_i \varepsilon_i$$

$$dU = dU(0) + \sum_i n_i d\varepsilon_i + \sum_i \varepsilon_i dn_i$$

In the absence of all changes other than heating,

$$dU = \sum_i \varepsilon_i dn_i$$

We know about that, that whenever you want to determine the internal energy, you find out the total energy and add a constant to this. When I write this as equal to U (0) plus summation i n_iE_i. Now, I am talking about how many molecules are there in a state of energy E i. Now let there be some change. What I will write is dU is equal to dU (0) plus summation i n_i E_i plus summation i E_i dn_i.

Concentrate on this equation. What I have just done is, I have considered the upper equation U is equal to U (0) plus summation n_i d_i.

Let the system undergo some change, then du is equal to dU (0) plus summation n_i dE_i plus summation E_i dn_i. Note down that this is constant, U (0) is constant, so dU (0) should vanish, it should become 0. Now, we need to figure out that which other term remains or do both the terms remain. First one is changes in energy dE_i, second is changes in the number of molecules in i thstate. To understand this, let us take a look at this figure.

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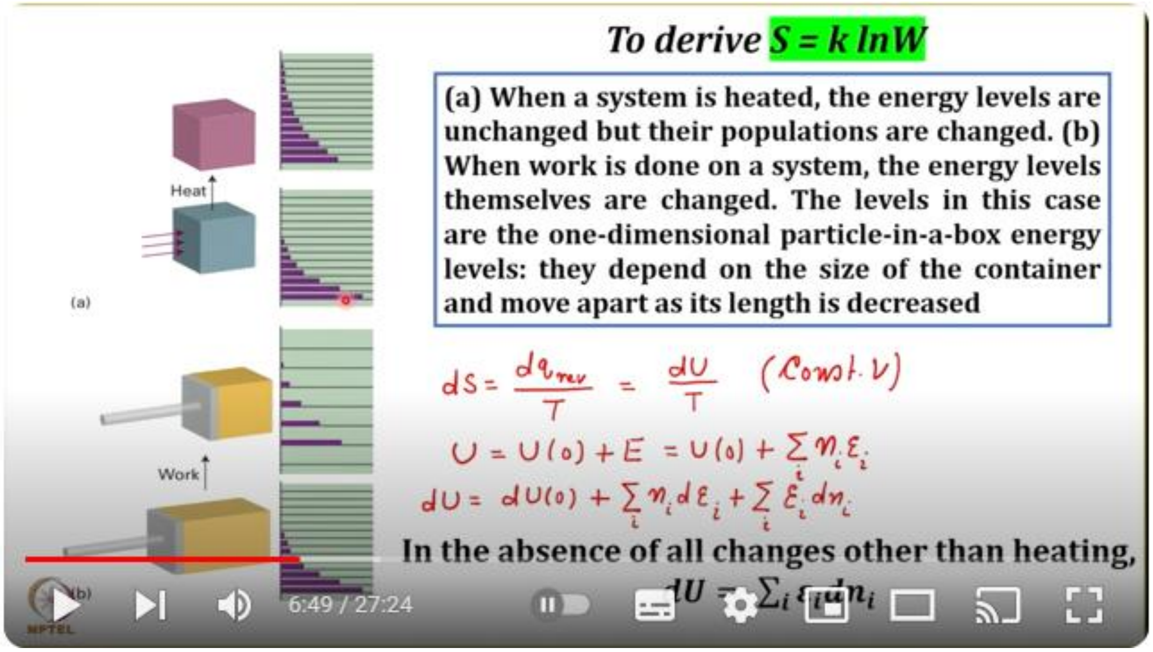

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Let us first concentrate on this figure A. Consider this spread out of energy states or energy levels and the population. Let us supply some heat to the system. We are connecting dS with heat. Once, you heat a system.

Once you heat a system, what is happening is the population is changing. And second, is you work, work on a system, working in such a way that you are changing the length, you are changing the dimensions of the box. If you do that, if you change the dimension or the size of the container, the length is affected. And remember that the energy levels are connected with the length and then the energy levels will be affected. But the case that we are discussing, you are providing heat that does not alter the energy levels. It may alter the population. So, therefore, what is going to happen now? This one is going to vanish and there is no change in the energy states. So, dE_i that also should vanish. dE_i is equal to 0. The term that will remain is this one, summation E_i dN_i. So in the absence of all changes other than heating, this is important to note down. What we are talking about here is in the absence of all changes other than heating, we just establish that dU is equal to summation E_i dN_i. So, we have to note over here that we got an expression for dU and we just showed in the beginning that dU is connected to change in entropy. That means what is dS? dS is equal to simply dU by T. We will make use of this now.

Let us do that. We want to derive an expression that connects entropy with the weight of the most probable configuration of the system. That is S is equal to K log W. This is our next goal establishing this relationship between entropy and log W. We will get into the derivation soon, but if you just look at this expression, what does it tell?

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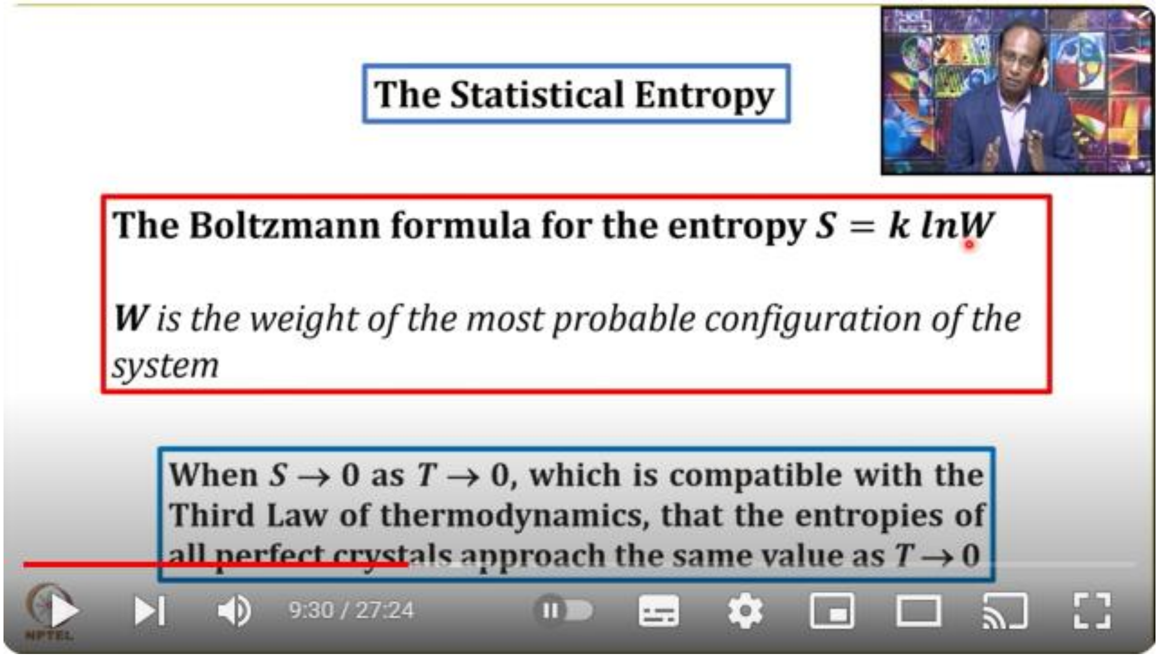

The Statistical Entropy

The Boltzmann formula for the entropy $S = k\, lnW$

***W** is the weight of the most probable configuration of the system*

When $S \rightarrow 0$ as $T \rightarrow 0$, which is compatible with the Third Law of thermodynamics, that the entropies of all perfect crystals approach the same value as $T \rightarrow 0$

That when the temperature approaches 0, let us say, that means all the molecules then you will find that are most are in the ground state. If all the molecules are to be found in the ground state, there is only one way that configuration can be achieved. That means in that case, W is approaching 1. If W approaches 1, log W approaches 0. That means when S approaches 0, as T approaches 0, which is compatible with the third law of thermodynamics that the entropies of all perfect crystals approach the same value as T approaches 0. If you read this statement very carefully, it says approach the same value as T approaches 0 and it does become 0 for perfectly crystalline substances. Let us start discussing the derivation.

What we have, we just wrote that dU is equal to summation i E_i dn_i and we also showed that dS is equal to dU by T. We are putting the constant volume condition. That means dS, I can write this as 1 upon T summation i E_i dn_i. I am making use of this definition dS is equal to dU by T. Now remember that β is equal to 1 over KT. This means 1 over T is equal to K times β. I can use that. What do I have now? dS is equal to instead of 1 over T, I will write K β summation i E_i dn_i. You will soon realize that why I am doing these kinds of transformations.

Let us rearrange this. I will keep K outside and I will take β inside β E_i dn_i and just keep in mind that we have to keep most probable configuration in mind. You remember that when we derived the Boltzmann distribution, we went through a certain procedure where we used Lagrange's method of undetermined multipliers to set one term equal to 0. Let me write that. At that time, remember that we derived this kind of expression δ log W δ n_i plus α minus β E_i.

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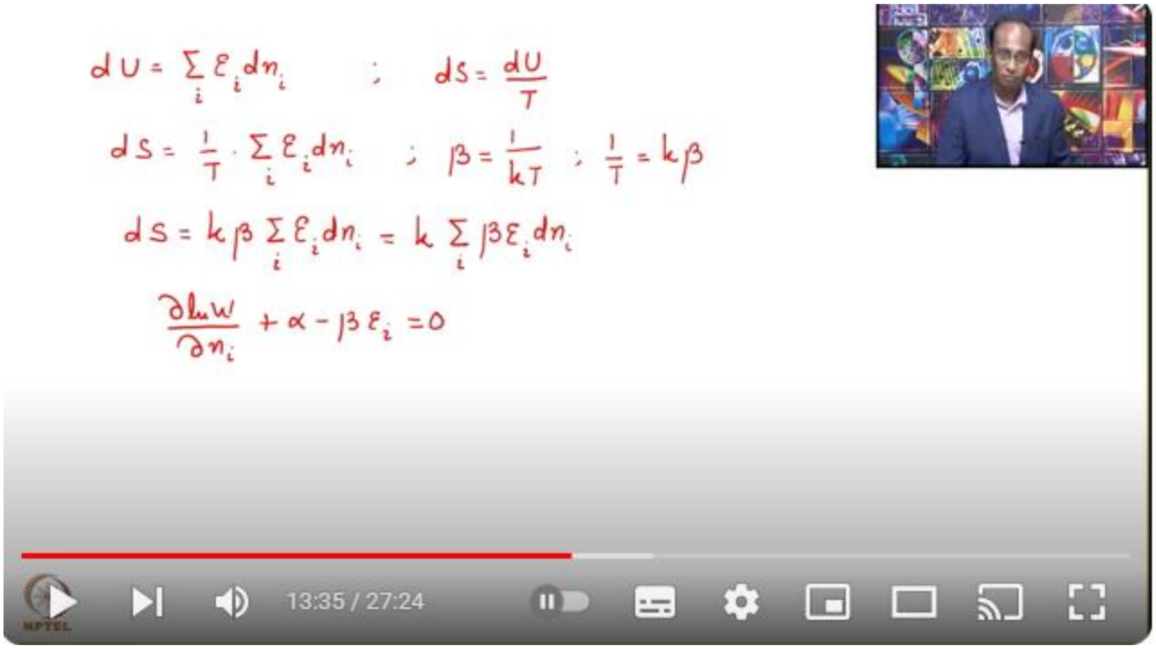

$$dU = \sum_i \varepsilon_i dn_i \quad ; \quad dS = \frac{dU}{T}$$

$$dS = \frac{1}{T} \cdot \sum_i \varepsilon_i dn_i \quad ; \quad \beta = \frac{1}{kT} \quad ; \quad \frac{1}{T} = k\beta$$

$$dS = k\beta \sum_i \varepsilon_i dn_i = k \sum_i \beta \varepsilon_i dn_i$$

$$\frac{\partial \ln W}{\partial n_i} + \alpha - \beta \varepsilon_i = 0$$

We had set this equal to 0 in order to find most probable configuration. Then after that, we have worked for obtaining an expression for α and obtaining an expression for β. From this expression, what I have? β E_i is equal to δ log W δ ni plus α and now I can substitute β E_i over there. So, what do I have now? ds is equal to K summation i δ log W δ n_i plus α and I have dn_i. Let us further expand this. I have now ds is equal to K summation i δ log W δ$n_i dn_i$ plus K summation i α dn_i which I can further now simplify.

I have K δlog W δ n_i with this summation dn_i. This is first term plus K times α summation i dn_i. Now let us carefully examine what we have done. We have now two expressions over here. The first one is K δ log W δ n_i dn_i.

Second one is K α into summation dn_i. Sum of all the changes has to be 0 because the total number of molecules is constant. Therefore, this term summation i dni that has to be 0 because total number of molecules is constant. Therefore, if the population in the ground state is decreasing, it must increase by equal amount in the upper excited states. Therefore, we can set this equal to 0.

After you set that equal to 0, I have the expression ds is equal to K summation iδ log W δ n_i dn_i because the other part is set equal to 0. Summation i dn_i is set equal to 0. Now let us try to recognize this expression.

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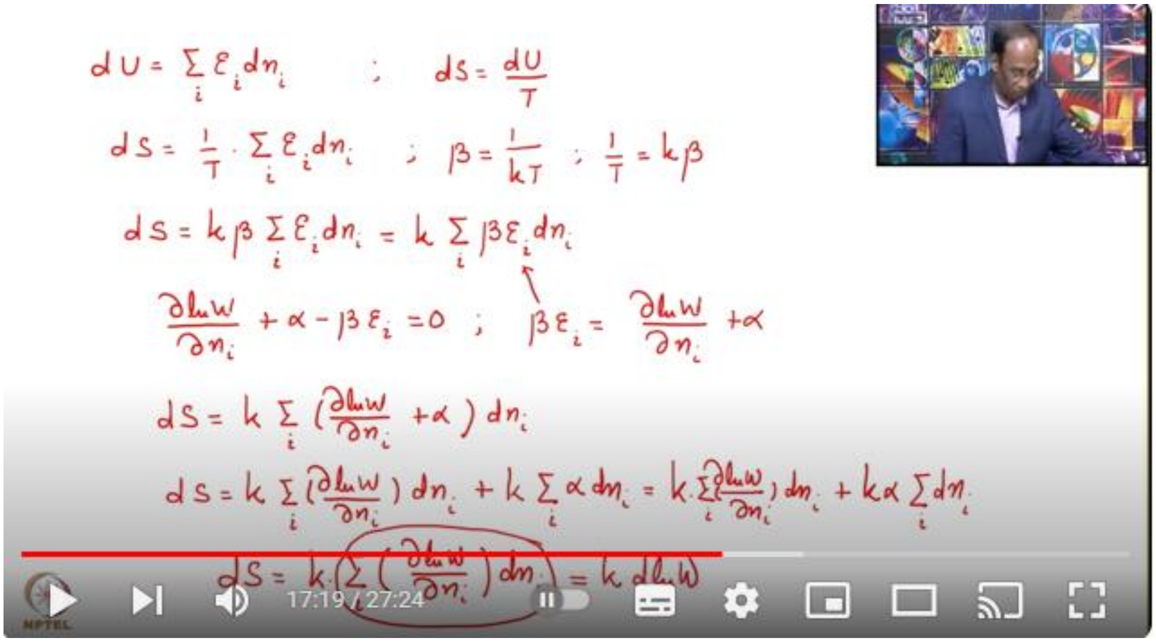

$$dU = \sum_i \varepsilon_i dn_i \quad ; \quad dS = \frac{dU}{T}$$

$$dS = \frac{1}{T} \cdot \sum_i \varepsilon_i dn_i \quad ; \quad \beta = \frac{1}{kT} \quad ; \quad \frac{1}{T} = k\beta$$

$$dS = k\beta \sum_i \varepsilon_i dn_i = k \sum_i \underset{\uparrow}{\beta\varepsilon_i} dn_i$$

$$\frac{\partial \ln W}{\partial n_i} + \alpha - \beta\varepsilon_i = 0 \quad ; \quad \beta\varepsilon_i = \frac{\partial \ln W}{\partial n_i} + \alpha$$

$$dS = k \sum_i \left(\frac{\partial \ln W}{\partial n_i} + \alpha\right) dn_i$$

$$dS = k \sum_i \left(\frac{\partial \ln W}{\partial n_i}\right) dn_i + k \sum_i \alpha\, dn_i = k \cdot \sum_i \left(\frac{\partial \ln W}{\partial n_i}\right) dn_i + k\alpha \sum_i dn_i$$

$$dS = k \cdot \boxed{\sum \left(\frac{\partial \ln W}{\partial n_i}\right) dn_i} = k\, d\ln W$$

Let's transfer back to our previous discussion. This was dlog, W k dlog W. Remember when we discussed that log W as a function of n_0, n_1, n_2, n_3, etcetera, then we wrote that expression that d log W is equal to δlog W by δn_i into dn_i summation i. Let us remember this equation. What we have done is that we have come up with an expression dS is equal to k into d log W. That is the expression that we have come up with. This upon integration strongly suggests that this expression will take a form S is equal to k log W, where W is the weight of most probable configuration.

If we know the weight of most probable configuration and the value of the Boltzmann constant, it should be possible to find out the entropy of a system. We talked about that if W approaches a value of 1, log W approaches a value of 0. In that case, s approaches a value of 0. And this is possible when temperature approaches a value of 0. When temperature approaches 0, I am again repeating what I just discussed in the previous slides. When temperature approaches 0, the molecules are going to be in the ground state. And in how many ways you can arrange that, what is the most probable configuration? W is going to be only 1 because there is only one way you can have that configuration when all the molecules are in the ground state.

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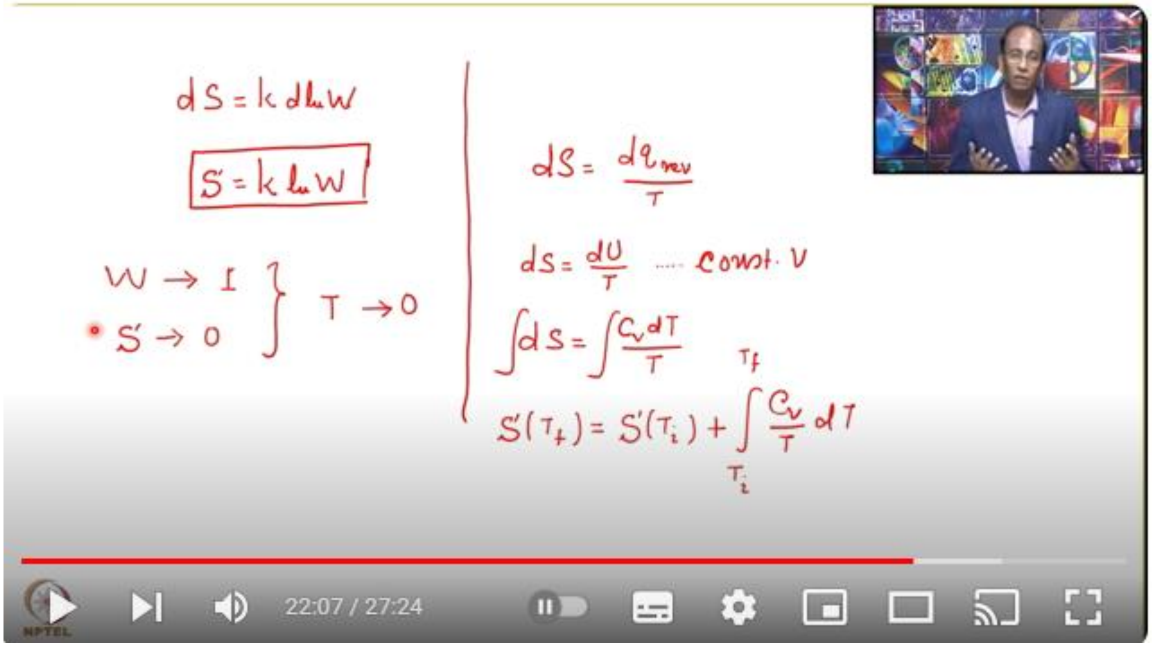

$$dS = k\, d\ln W$$

$$\boxed{S = k \ln W}$$

$$\left.\begin{array}{l} W \to 1 \\ S \to 0 \end{array}\right\} T \to 0$$

$$dS = \frac{dq_{rev}}{T}$$

$$dS = \frac{dU}{T} \quad \text{..... const. } V$$

$$\int dS = \int \frac{C_v\, dT}{T}$$

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_v}{T}\, dT$$

So therefore, when temperature approaches 0, W approaches 1 and if W approaches 1, log W approaches 0 and your entropy approaches 0 and this is true for perfectly crystalline substances. A small comparison with the results that we obtained from chemical thermodynamics can be made. In chemical thermodynamics, you remember that this expression dS is equal to dq_{rev} by T at constant volume or at constant pressure. Let us say we keep constant volume. Then dS will become dU by T. This one is possible at constant volume or I say dS is equal to C_v dt by T. Now integrate T_i to T_f. So S at T_f is equal to S at T_i plus integration T_i to T_f C_v by T dt. This is a constant volume and if you keep constant pressure, then instead of C_v, it will be C_p.

You can compare here how we get the information about the entropy at different temperatures. In order to use the concepts of chemical thermodynamics, classical thermodynamics, the temperature dependence of the entropy is connected with the heat capacity depending upon whether your constraint is constant volume or your constraint is constant pressure. And whereas, when you talk about the concepts of statistical thermodynamics, there you are talking about the weight of a configuration. As the temperature changes, the instantaneous configurations will change. If the instantaneous configurations change, then we have to find out the weight of the most probable configuration. Let us take an example, the example of perfectly ordered system HCl. Why I am saying perfectly ordered system is that in this you can notice that all the hydrogens, for example, hydrogen and chlorine, hydrogen and chlorine, hydrogen and chlorine, all the arrangement in a perfectly ordered manner. And let us apply this definition, S is equal to k log W. When the temperature approaches 0, this arrangement which is shown here on the screen is going to give the minimum energy configuration. Only this arrangement, that means, weight of the configuration is 1.

That means, only one way, this is the only one way of arranging HCl in the crystal to obtain minimum energy conformation. So, when you get W equal to 1 as T is equal to 0, then S is equal to K log 1 which is equal to 0. And the reason that why only this configuration leads to minimum energy confirmation is due to the large electronegativity difference between H and Cl. What I mean is that if instead of HCl, you make it ClH, then the energy of the crystal will change. Similarly, if you take another example, let us say I take the example of carbon monoxide.

And here, the molecular dipole moment of CO is very small. That means, whether in the crystal you have CO or OC, you see the orientation is changed. But this change in orientation does not lead to change in the energy of the crystal. That is either of the two orientations possible with virtually the same energy. That means, CO or OC, the molecule can arrange in two possible configurations.

There are two orientations which lead to the same energy. So, if there are N molecules, then W is equal to 2 raised to the power N. For one molecule, W is equal to 2 which leads to the same configuration. For N molecules, W isThermo equal to 2 raised to the power N. Substitute W equal to 2 raised to the power N and solve it. You have Nk log 2 or Nr log 2 which leads to a value of 5.76 joules per kelvin per mole even at absolute 0. So, by using the definition of statistical thermodynamics, you can calculate the entropy at absolute 0. I once again refer back to the definition of third law of thermodynamics. It says that entropy of each substance is positive which may become 0 at absolute 0 and it does become 0 for perfectly crystalline substances. This particular example of CO is not of a perfectly crystalline substance because there is a configurational disorder even at absolute 0. And from the knowledge of the weight of a configuration, here CO or OC, two possible configurations. So, for N molecules, the weight is 2 raised to the power N. There is some value of entropy even at absolute 0 and this entropy has some meaning which we will discuss later on. For the time being, let us remember that S equal to K log W can be used to calculate the entropy of a system provided we know the information on the weight of the configuration or weight of the most probable configuration. We have now connected S with W. Next, we will connect entropy with the molecular partition function in the next lecture. Thank you very much.