Fundamentals of Statistical Thermodynamics

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Lecture - 02

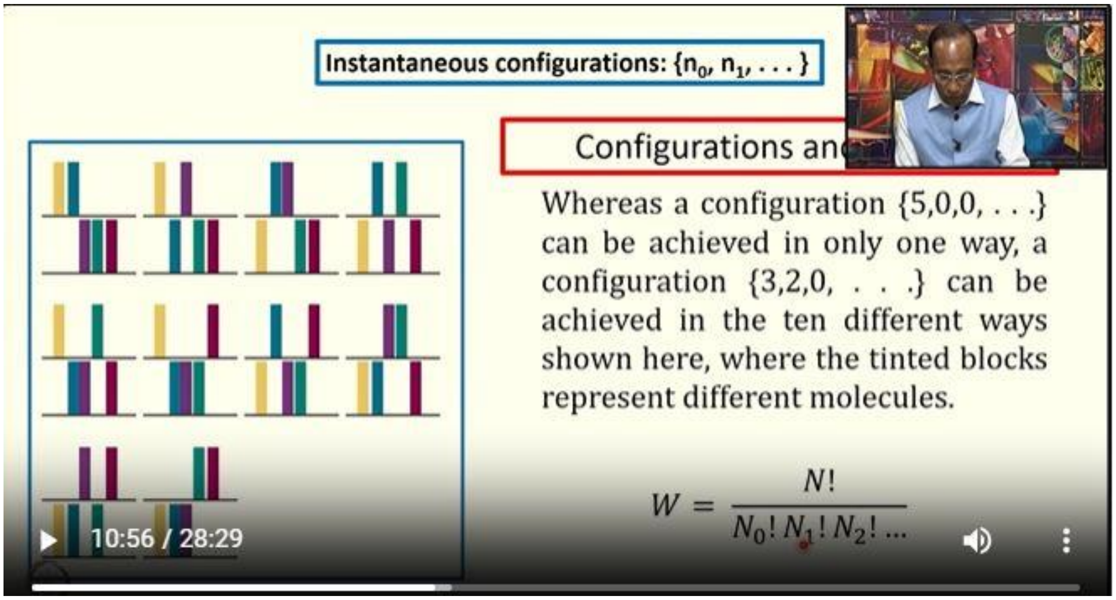
Welcome back to the next lecture of Statistical Thermodynamics. We have been discussing the various essential points which are required before we start developing further concepts and further equations. In the previous lecture, we discussed about configuration and weights. We started discussing about the configuration and weights and there we talked about that the molecule may exist in various energies, energy states, and most importantly what we discussed was that E_0 we are setting equal to 0. But that does not mean that the internal energy which is equal to the sum of total energy you know possessed by the molecule in all forms. Because what we talked about that in order to obtain actual internal energy U, we may have to add a constant to the calculated energy system and we also took an example like if we are considering the vibrational contribution like you know if you are talking about the oscillators then in order to obtain internal energy then we have to add the total zero point energy of any oscillators in the sample.
So, let us keep in mind that if somehow we are able to calculate the total energy and if we want to now calculate the internal energy from the total energy we will need to add a constant which is equal to the zero point energy of that system. Now let us start talking about what is meaning by configuration and what is the meaning by weight of a configuration. We will start first talking about instantaneous configuration. Please note the way this instantaneous configuration is written n_0, n_1 so on so on and so on.
The system is having total of n molecules . Let me point out. Let us say I talk about the instantaneous configuration of a system if there are total of n molecules. These n molecules they can you know n_0 molecules can arrange in some energy state n_1 can occupy some other energy state this capital N is equal to sum of n_0, n_1, n_2 etcetera that is the summation of all these n's is equal to capital N. Let us discuss this in a little more details. I am saying that n is equal to n_0 plus n_1 plus n_2 plus so on and the instantaneous configuration. How do I interpret this instantaneous configuration? The way to interpret this instantaneous configuration is that there are n_0 number of molecules in a state of energy E_0, n_1 number of molecules in a state of energy E_1, n_2 number of molecules in a state of energy E_2. So therefore, how much is the energy of this state? This one the total energy will be n_0 times E_0. Here the total energy will be n_1 times E_1. Here the total energy is n_2 times E_2 and so on.

Sum of all these will be total energy. I repeat what is the meaning of instantaneous configuration? This the way I have written n_0, n_1, n_2 etcetera etcetera. The way to interpret this is there are n_0 number of molecules in a state of energy or in a level where the energy is E_0. The second one, is in an energy state E_1, n_2 is n_2 number of molecules or particles whatever you are considering in a state of energy E_2. So therefore, remember this concept of instantaneous configuration and the way to read instantaneous configuration. Obviously, when I talk about n_0 into E_0, E_0 we are always setting equal to 0.

Remember the previous lecture that we set the ground state energy equal to 0. Therefore, this is 0, n_0 into E_0 whatever the number is it is 0. This energy is n_1 E_1. This energy is equal to n_2 E_2. So the total energy will be the sum of all these. All right. Now let us talk about an instantaneous configuration corresponding to 5, 0, 0. How do we read it? The way we read it is that there are 5 particles or 5 molecules in the ground state or in a state with energy equal to E_0. Everything you know all the 5 molecules are in the ground state and there is no molecule which is in the excited state. So this 5, 0, 0 can be achieved only in one way.

And what is that one way? Is that all the 5 molecules are in the ground state. Now if you look at the second instantaneous configuration 3, 2, 0, etcetera, etcetera. The total number of molecules is 3 plus 2 equal to 5. But there are 3 molecules in the lowest energy state and 2 molecules are in the first excited state.

Total of 5. Obviously, the upper one can be achieved in more number of ways. Okay. Although here I write can be achieved in 10 different ways, you can see over here that 3, 2, 0, 3 molecules in the ground state. You can look at here 3. You can look at the color code. You know here the violet one is first and here the violet one is in the end. Here the violet one and the other combinations are different. But these all molecules, all particles they are indistinguishable, they are independent. And these can be, these 3, 2, 0 configurations can be achieved if you look at the total. There are 10 different ways. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10. And in each one you can see the color coding the molecules are arranged in a different way. So, therefore, we have to find out the number of ways of achieving a configuration number of distinguishable ways. And a formula which we are soon going to discuss which can be used to determine the weight of a configuration, we will actually show a short derivation of this, is given by n factorial. What is this n? n is the total number of molecules.



$$W = \frac{N!}{N_0!\,N_1!\,N_2!\,...}$$

In this case, it is 5. n_0 factorial, n_0 factorial is in the ground state that is there are 3, 3 factorials. This is n 1 is 2 factorials. Then 0 factorial etcetera, etcetera. So this is the formula which we are going to use and I am going to discuss this formula in a little bit more details. Let us consider an arrangement which is let me just put a bar over here. I have n_0. This is one instantaneous configuration. Now let us say I have another one where two molecules are excited to the first excited state. These two instantaneous configuration. And let us discuss that out of these two which one can be achieved in more number of ways. Let us discuss about that. The first one, how many ways one can achieve this instantaneous configuration? There is only one way because the requirement is here that all the molecules, all the particles are in the ground state and there is nothing in the excited state. So there is only one way this configuration can be achieved. Now, let us talk about the second one.

Two molecules have been picked up from the ground state and pushed into the first excited state. Let us discuss now how many ways we can achieve this kind of configuration. Okay. Initially, we have n particles. So, I can pick up you know I have to pick up one molecule and take it to the first excited state.

I have n choices. Right. So, let us say I take up one and put it in the first excited state. I had n choices. I could pick up from this n number of molecules. Now how many are remaining? There are n minus 1 because 1 has been picked up and put into the first excited state. Now in order to choose the second one, there are how many choices? n into there are how many choices? n minus 1 because there are n minus 1 particles and n minus 1 molecules remaining there. So, therefore, the total number of choices when I combined everything is n into n minus 1. because the first one could be picked up amongst n. The second one can be picked up amongst n minus 1. Therefore, the total number of ways you can achieve this second one n minus 2 2 0 0 instantaneous configuration is n into n minus 1. But, remember one thing. We have been talking about the particles. We have been talking about the molecules which are not distinguishable. So, you cannot distinguish between let us say a jack and a jade. The first molecule and the second molecule all are same. Their properties are same. Their look is same. So therefore, when you want to pick up a molecule from the first one that is n molecules, you want to pick up one. There are n different ways and you want to pick up second. There are n minus 1 different ways. Which one out of the two is picked up whether the first one or the second one, it will lead to the same configuration. It will lead to the same state. So therefore, if we do not want to over count the number of states, we must divide by a factor because we are talking about two molecules. Whichever one you want to pick up one, whichever it does not matter out of these two. Therefore, it must be divided by a factor of 2. Only half of the configurations will be distinguishable. Only there will be half of n into n minus 1 ways of achieving a distinguishable configuration.

Therefore, the second one here, this configuration can be achieved in n into n minus 1 divided by 2. These are many number of ways. Therefore, any configuration which can be achieved in more number of ways is a more dominating configuration. That means if a system is allowed to be in these two states $n_{0\ 0}$ or n minus 2 2 0 0, the system will most likely be found in the second one because it can be achieved in more number of distinguishable ways. While we are discussing this, remember that I am not imposing the energy criteria over here because just think about what is the total energy of this instantaneous configuration. The total energy will be n into 0. It's a ground state. We are setting energy equal to 0. That means total energy is 0 over here and the total energy here is n minus 2 into 0 plus 2 into E 1. So, for the argument's sake here, please ignore that energy criteria over here. Just concentrate on the number of ways you can achieve an instantaneous configuration. We will bring in the energy criteria energy restriction a bit later. A system can exist in several instantaneous configurations because, under the given conditions at a given temperature, the system can be in different instantaneous configurations. For example, instead of n minus 2 2 0, it can be n minus 5 3 2 0 0 etcetera etcetera. There can be several instantaneous configurations.

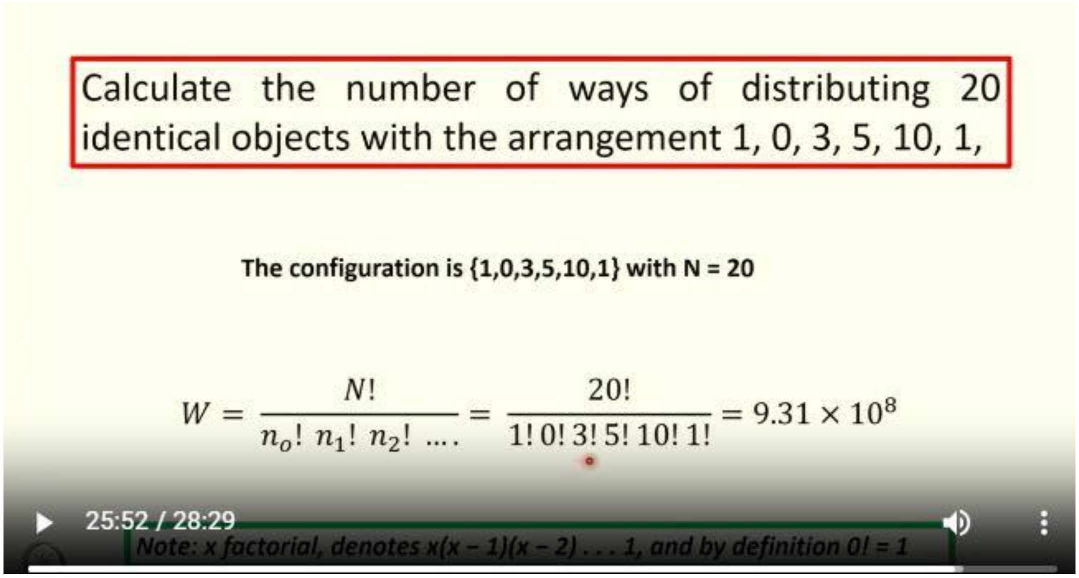
So don't get confused by that. So, a general instantaneous configuration n 0, n 1 etcetera, this can be achieved in w different ways and we are calling this w as the weight of the configuration and this weight of configuration we will soon discuss in detail that it can be written as n factorial divided by n_0 factorial, n_1 factorial, n_2 factorial. This n is the sum of all these small ns' and n_0, $n_{1,}$ n_2 etcetera come from the instantaneous configuration. So, please keep this in mind. Now let us discuss by taking that let us say there are 18 molecules or if you don't want to consider 18, you just consider there are n molecules and there are different bins. Consider these compartments as different bins and these 18 molecules are to be distributed in these different bins.

Let me represent these molecules as balls. There are balls, there are bins and these n balls which in this case we are considering as 18 are to be distributed in different bins. So, in order to choose the first one, I take the first one, there are n balls available, the second one there are n minus 1 balls available, for the third one, there are n minus 2 balls available. So in the same arguments let me go that there are total n balls available. When I pick up select the first one, I have n choices. When I select the second one, there are n minus 1 choice.

When I select the third one, there are n minus 2 choices. Eventually when we finally end up with only one choice and this is nothing but n factorial. There are n factorial ways you can pick up a ball and put into different bins. Now let us classify these bins separately. Let us say this bin has some energy E0, this has let us say E_1, this has E_2, this has E_3, etcetera, etcetera or they are different bins. And let us say we put three balls into this and you cannot distinguish it between these balls. How many ways these balls can be arranged here? Three factorial, right. How? If I classify this as a, b, c, then I can have a c b, b c a, b a c, c b a, c a b, and so how many? 1, 2, 3, 4, 5, 6 which is equal to 3 factorials. Similarly, if there are if I put if six balls are there in this designated bin, then there are six factorial ways the ball can be picked up. And each arrangement reduces the total weight of a configuration because you want to calculate the number of distinguishable arrangements.

So here is how we will calculate the distinguishable arrangements. We have this n factorial, here n is equal to 18, so I will put 18 factorials. Okay. And then divided by 3 factorials into 6 factorials into 5 factorial into 4 factorial, 3 factorial into 6 factorial, 5 factorial, 4 factorial. I hope it is clear that you want to calculate the number of distinguishable arrangements. This will be equal to n factorial divided by the factorial of each number which represents the number of particles or number of molecules in a given energy state.

So, what I was talking about is this formula W is equal to n factorial divided by n 0 factorial, n_1 factorial, n_2 factorial, etcetera. Let us now solve a problem.



$$W = \frac{N!}{n_o!\, n_1!\, n_2! \; \ldots.} = \frac{20!}{1!\,0!\,3!\,5!\,10!\,1!} = 9.31 \times 10^8$$

The problem is to calculate the number of ways of distributing 20 identical objects, remember this keyword identical objects, with the arrangement 1, 0, 3, 5, 10, 1. And if I were to write instantaneous configuration, I will write like this 1, 0, 3, 5, 10, 1. That means there is 1 molecule or 1 particle in the ground state, there is nothing in the first excited 3 in the second excited so on and so on. And sum of all these 1 plus 3 is 4, 4 plus 5 is 9, 9 plus 10 is 19, and 19 plus 1 is 20 so n is equal to 20. And we have to calculate the number of ways of distributing these 20 identical objects with the arrangement given to us. So, straight forward n is equal to 20, so 20 is factorial and we can pick up n_0, n_1, n_2, etcetera from this instantaneous configuration and write and then calculate the number comes out to be 9.31 into 10 to the power 8. Look at this very high number, the number of ways these 20 identical objects can be arranged.

Now as I just mentioned that this instantaneous configuration can change depending upon the factors, depending upon the conditions. You change the temperature; the instantaneous configuration will change. Even under the given conditions, there can be several instantaneous configurations possible. But, just for the numerical problem-solving sake, note here that x factorial denotes x into x minus 1 into x minus 2 so on until you reach 1 and by definition 0 factorial is equal to 1. So, these please keep in mind. So now, if there are several instantaneous configurations and there can be weight of a configuration, how do we proceed then? In which state or in which configuration your system is going to be most likely in? That needs to be further discussed. We will further develop concepts towards that, that is to find out a configuration in which the system is most likely going to be there and then further develop the concepts of statistical mechanics or statistical thermodynamics based on those. Thank you very much.