Fundamentals of Statistical Thermodynamics

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Lecture - 09

Numerical Problems Set-I (based on partition function)

Today, we are going to discuss applications of the concepts, which we have developed so far. We have derived some expressions, for example, expressions for writing the partition function, and expressions for fractional population of any i^{th} state. And in today's discussion, we will solve some numerical problems and then we will try to understand what these results represent. So let us get started with the first numerical problem. The first problem, the first question that I want to discuss with you today is that in broad sense, how do the concepts of statistical thermodynamics differ from chemical thermodynamics? Explain by taking an example. This is just a discussion-based problem, numerical problems we will discuss ahead, but the question that is being asked over here is that in a broad sense, in a general sense, how does statistical thermodynamics differ from chemical thermodynamics? Going back to our previous discussion, in chemical thermodynamics we deal with the average properties, we deal with the bulk properties. And in statistical thermodynamics, we deal with the molecular properties. We also discussed that statistical thermodynamics provides a link between molecular properties and bulk thermodynamic properties. Let us take an example. Let us take an example of pressure of a gas. Pressure of a gas, let me represent by P. What is P? P is force per unit area. Consider a gas contained in a cylinder. How do we define the pressure of the gas over there? It is the force exerted by the molecules per unit area. Remember that in a container, the gas molecules are colliding with each other.

So therefore, whatever the energy possessed by the molecules that is being exchanged, they are not just colliding with each other, but the energy is also being distributed between different modes of motion. We have discussed this earlier. Now you see how my discussion is changing from an average quantity which is the pressure, which is the force per unit area. It is an average quantity we are talking about. And then I am talking about that there are different molecules, they are colliding with each other, the energy is getting distributed amongst themselves, not only getting distributed amongst themselves but also between different modes of motion. So this is how the concepts of chemical thermodynamics differ from statistical thermodynamics. In chemical thermodynamics, we talk about bulk properties, average properties. Whereas in statistical thermodynamics, we start talking about individual molecules, we talk about the population of different energy levels, and then we connect with the thermodynamic quantities. So therefore, once again reemphasizing what is statistical thermodynamics is a link between other properties and bulk thermodynamic quantities or properties. So this is how in a broad sense the concepts of statistical thermodynamics differ from chemical thermodynamics.

Now let us move to another question. Read the question or try to understand the question carefully. The question is, consider a system of 20 non-interacting molecules, which means I am talking about 8 molecules or independent molecules with a uniform ladder of energy levels, each separated by 100 centimeter inverse. How many out of the following instantaneous configurations are simultaneously possible? Justify your answer with suitable calculations.

Let us try to understand the question.

Consider a system of 20 non-interacting molecules with a uniform ladder of energy levels and each separated by 100 centimeter inverse. So what I have is, I have a uniform ladder of energy level and each one is separated by 100 centimeter inverse. Let me represent that 100 centimeter inverse by E. So each one, for example, if this is E_0, this is E, this is 2E, this is 3E, this is 4E and so on and this E separation is 100 centimeter inverse. And then we are asked, how many out of the following instantaneous configuration, what are those instantaneous configurations?

First one is 20, 0, 0, 0.

How do we read this? 20 molecules are in the ground state, that is with an energy equal to 0 and there is no molecule in the upper state. The second instantaneous configuration is, you have 10 molecules in the ground state, no molecule in the first excited state, 5 molecules in the second excited state, 2 in the third excited state, 0, 3, etcetera, etcetera and we already have learnt how to read an instantaneous configuration. And there are other instantaneous configurations given over here, like (2, 10, 3, 5, 0, 0) or 5, 5, 5, 5, etcetera, then (6, 10, 3, 5, 0, 0, 0, 0), etcetera.

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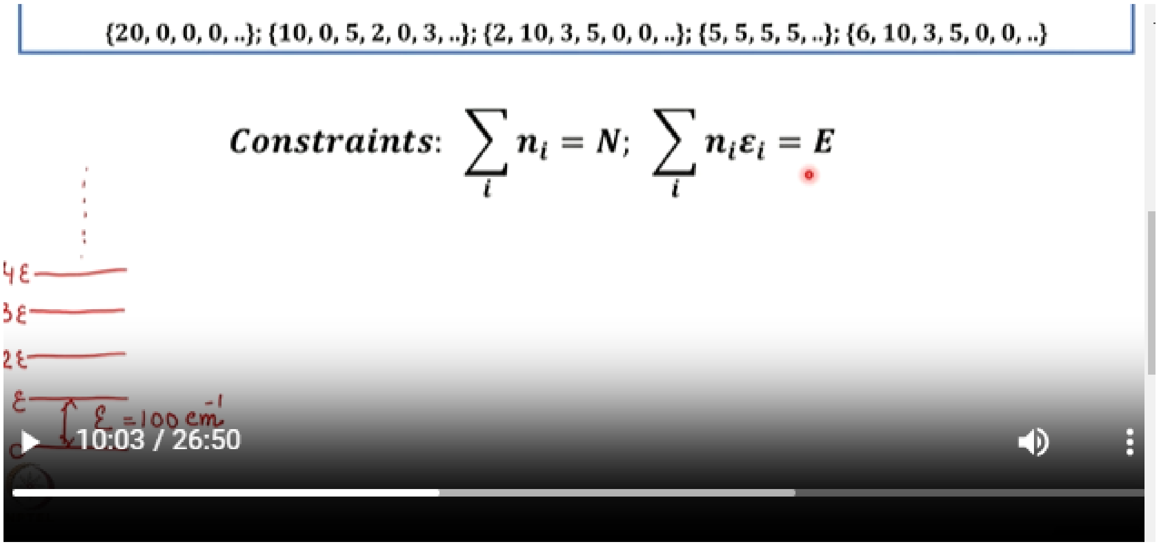

{20, 0, 0, 0, ..}; {10, 0, 5, 2, 0, 3, ..}; {2, 10, 3, 5, 0, 0, ..}; {5, 5, 5, 5, ..}; {6, 10, 3, 5, 0, 0, ..}

$$Constraints:\ \sum_i n_i = N;\ \sum_i n_i\varepsilon_i = E$$

The question is, how many out of the following instantaneous configurations are simultaneously possible? There can be several instantaneous configurations. But then, if you remember, we discussed that all the instantaneous configurations may not be permissible because certain constraints are there, certain laws, certain rules have to be followed.

What are those constraints? The first constraint is that the total number of molecules have to remain constant, that is, summation in$_i$ is equal to n. The molecules which are present in different energy state, the sum has to be equal to 20 because there are total 20 non-interacting molecules. And the second constraint is that the total energy of the molecules in each state has to be equal to the sum of that has to be equal to the total energy of the system. So, these two constraints have to be followed. One is summation n i is equal to capital N, that is, the total number of molecules and summation n_iE_i is equal to the total energy.

$$Constraints:\ \sum_i n_i = N;\ \sum_i n_i\varepsilon_i = E$$

So, therefore, let us now start working out for each system. Let us take the first instantaneous configuration. The first one is (20, 0, 0, 0,) etcetera. First of all, let us see that in each instantaneous configuration is this constraint follows, that is, the total number has to be 20. In this instantaneous configuration, it is 20 plus 0, 0, 0, 0, total is 20, fine. In the second one, 10 plus 5 is 15, plus 2 is 17, plus 3 is 20, that is also fine. Then 2 plus 10, 12, 12 plus 3 is 15, plus 5 is 20, that is also possible. 5 times 4 is 20, fine. Here 6 plus 10 is 16, plus 3 is 19, plus 5 is 24, that does not fit in, because that is not saying that summation n i is equal to N. So, therefore, this configuration is straight away ruled out. Now, we have to worry about the four instantaneous configurations. This constraint is followed by these four instantaneous configurations, first constraint. Now, we have to check about the second constraint. Let us start working about this. So, how much is the energy? Here, it will be, let us start writing down, the energy in this case is going to be 20 times 0, plus 0, plus etcetera, etcetera, right?

20 into, because they are all in the ground state, 20 times 0, 0 times whatever is the energy, etcetera, then the total value is equal to 0. Now, let us take the second one. Second one is 10, 0, 5, 2, 0, 3, this one, is 10, 0, 5, 2, 0, 3. Let us write the energy for this. This is equal to 10 times 0, plus 0 times E, plus 5 times 2E, then plus 2 times 3 times 0E, 2E, 3E, plus 0 times 4E, plus 3 times 5E, right. 0E, 2E, 3E, 4E, 5E. Let us see how much it comes to. This is coming to 10, plus 6 is 16, plus 15 is equal to 31 times E, where E is 100 centimeter inverse. Now, let us look at the third one. The third one is 2, 10, 3, 5, 0, 0, etcetera. Let us write the total energy for this. This is equal to 2 times 0, plus 10 times E, plus 3 times 2E, plus 5 times 3E, plus remaining all are 0, because 0, 0, 0. So, how much this comes to? 10, plus 16, plus 15 is equal to 31E. Now, let us look at the last one. We can utilize this space. Here we have 5, 5, 5, 5. So, energy is equal to 5 times 0, plus 5 times E, plus 5 times 2E, plus 5 times 3E, and the remaining are 0. So, how much this comes to? 5, plus 10, 15, plus 15, 30. Now, the answer is very clear. There are only two instantaneous configurations where the total energy is remaining the same. In other instantaneous configurations, for example, here it is 0 and here it is 30 times E.

E is 100-centimeter inverse. So, therefore, which instantaneous configurations are simultaneously possible? One is this, because this instantaneous configuration has a total energy of 31E, and the second instantaneous configuration which is simultaneously possible is this one. This also has a total energy of 31E.

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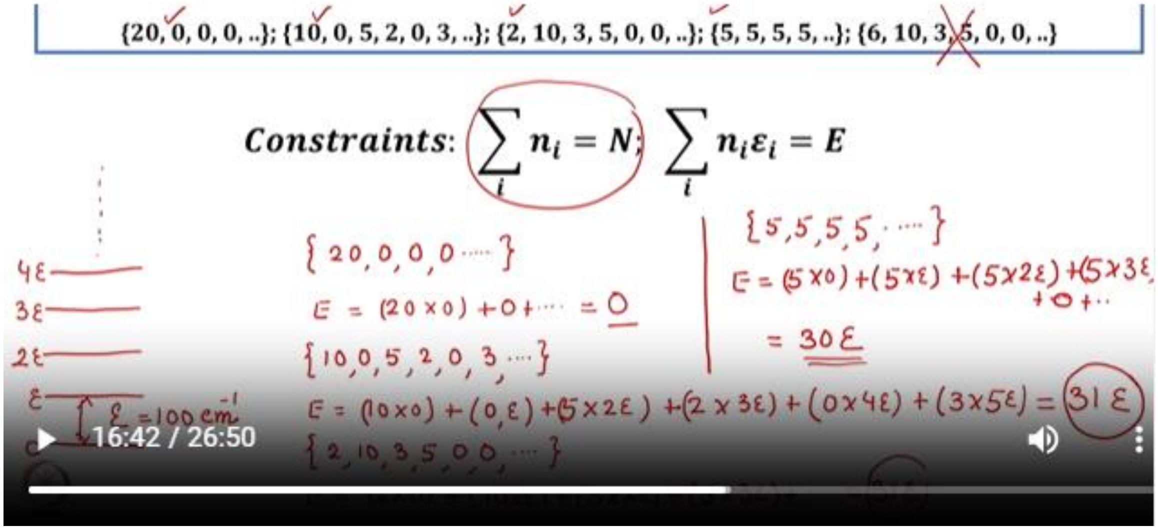

{20, 0, 0, 0, ..}; {10, 0, 5, 2, 0, 3, ..}; {2, 10, 3, 5, 0, 0, ..}; {5, 5, 5, 5, ..}; {6, 10, 3, $\cancel{5}$, 0, 0, ..}

Constraints: $\sum_i n_i = N$; $\sum_i n_i \varepsilon_i = E$

{20, 0, 0, 0 .....}

$E = (20 \times 0) + 0 + \cdots = \underline{0}$

{10, 0, 5, 2, 0, 3, ...}

$E = (10 \times 0) + (0, \varepsilon) + (5 \times 2\varepsilon) + (2 \times 3\varepsilon) + (0 \times 4\varepsilon) + (3 \times 5\varepsilon) = 31\,\varepsilon$

{2, 10, 3, 5, 0, 0, ...}

{5, 5, 5, 5, ...}

$E = (5 \times 0) + (5 \times \varepsilon) + (5 \times 2\varepsilon) + (5 \times 3\varepsilon) + 0 + \cdots$

$= \underline{30\varepsilon}$

That is 3100 centimeters inverse. And we already discussed that all these four instantaneous configurations 1, 2, 3, 4, their total number summation, they are following this summation ni is equal to n, 20. But the total energy constraint is only followed by this configuration and this configuration.

So, only two out of the given instantaneous configurations can exist simultaneously. So, remember that whenever you need to find out which different instantaneous configurations are simultaneously possible, then you need to follow these two constraints. But you remember our previous discussion. There are several instantaneous configurations are possible, but the system is most likely going to be found in an instantaneous configuration which has maximum weight. In this problem, we have only talked about which are the different instantaneous configuration.

Now you can always talk about the weight and then try to find out the system is most likely going to show the property of that instantaneous configuration which has maximum weight. Let us now switch over to another type of problem. Let us read this problem carefully. For a three level system in which different non-degenerate energy states are equally spaced by E, which out of the following expressions is correct for a fractional population of second excited state, show your derivation. So, we have to consider a three-level system in which different non-degenerate energy states are equally spaced. So, therefore, let us first draw. We draw a three-level system 1, 2, and 3. These are equally spaced. That means this is 0, this is E, this is 2E and we need to find out the expression for fractional population of the second excited state. So, let us recall what was the expression for writing fractional population. The expression for writing fractional population of ith state was n_i upon n is equal to exponential minus beta E_i upon q.

We will use this expression. The question that is asked is corresponding to a second excited state. So, this means the second excited state we are talking about is this one. Here for this E_i is equal to 2E and the q partition function is equal to ground state contribution is 1, second exponential minus beta E plus exponential minus 2 beta E. I have expanded q is equal to summation j exponential minus beta E_j. There is no question of degeneracy over here.

Therefore, g factor I have not included. Therefore, ni upon n which is P_i is equal to exponential minus beta EI. EI is equal to 2E, 2 beta E and q is 1 plus exponential minus beta E plus exponential minus 2 beta E. Let us take the logarithm on both sides. So, the logarithm of Pi is equal to log A by B is minus 2 beta E minus log this is 1 plus exponential minus beta E plus exponential minus 2 beta E.

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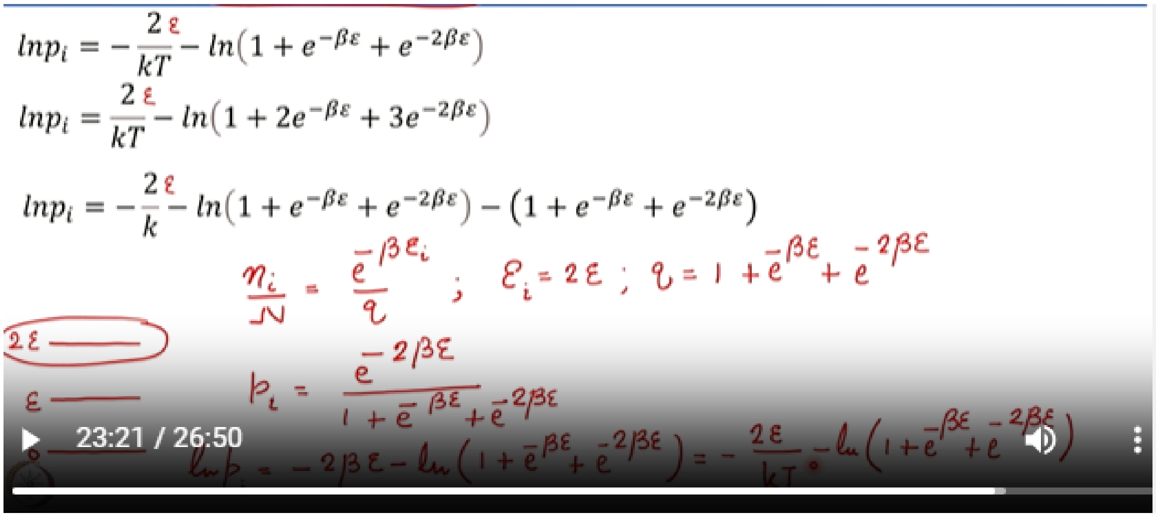

$$\ln p_i = -\frac{2\varepsilon}{kT} - \ln(1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon})$$

$$\ln p_i = \frac{2\varepsilon}{kT} - \ln(1+2e^{-\beta\varepsilon}+3e^{-2\beta\varepsilon})$$

$$\ln p_i = -\frac{2\varepsilon}{k} - \ln(1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}) - (1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon})$$

$$\frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{q} \; ; \; \varepsilon_i = 2\varepsilon \; ; \; q = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}$$

$$p_i = \frac{e^{-2\beta\varepsilon}}{1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}}$$

$$\ln p_i = -2\beta\varepsilon - \ln(1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}) = -\frac{2\varepsilon}{kT} - \ln(1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon})$$

Beta is equal to 1 over KT. This is equal to minus 2E upon KT minus log 1 plus exponential minus beta E plus exponential minus 2 beta E. Let me write here E. So, therefore, what we have got is the logarithm of the fractional population is minus 2E upon KT minus log of 1 plus exponential minus beta E plus exponential minus 2 beta E. So, therefore, the first one is the correct expression. The way to solve this kind of problem is first of all we need to understand that how different energy levels or different energy states are arranged organized. It is possible that some of the states may have the same energy and if different states have the same energy those states will form a level. Therefore, a particular energy level may be g fold degenerate. We have been expressing degeneracy in terms of g and suppose if there are more than states more than one state which have the same energy then the fractional population of that level is going to be g fold. Suppose, if I consider this expression and if ith state is two-fold degenerate that means the population of that energy level is going to be twice of that of a one state then in that case that g factor needs to appear here and kind of you know will modify this kind of expression, but that we are going to discuss in the next set of numerical problems. So, the take-home lesson from the discussion on these questions is that we should be able to write expression for the partition function.

Expression for partition function if there are discrete energy levels which are given to us like uniform ladder of energy level or some sequence of energy levels we should be able to write expression for partition function and then we should be able to write expression for fractional population. Once we are able to write these kind of expression you will see in the lectures which we are going to now discuss ahead it will be easier to connect the partition function with different thermodynamic quantities.

Thank you very much.