Fundamentals of Statistical Thermodynamics

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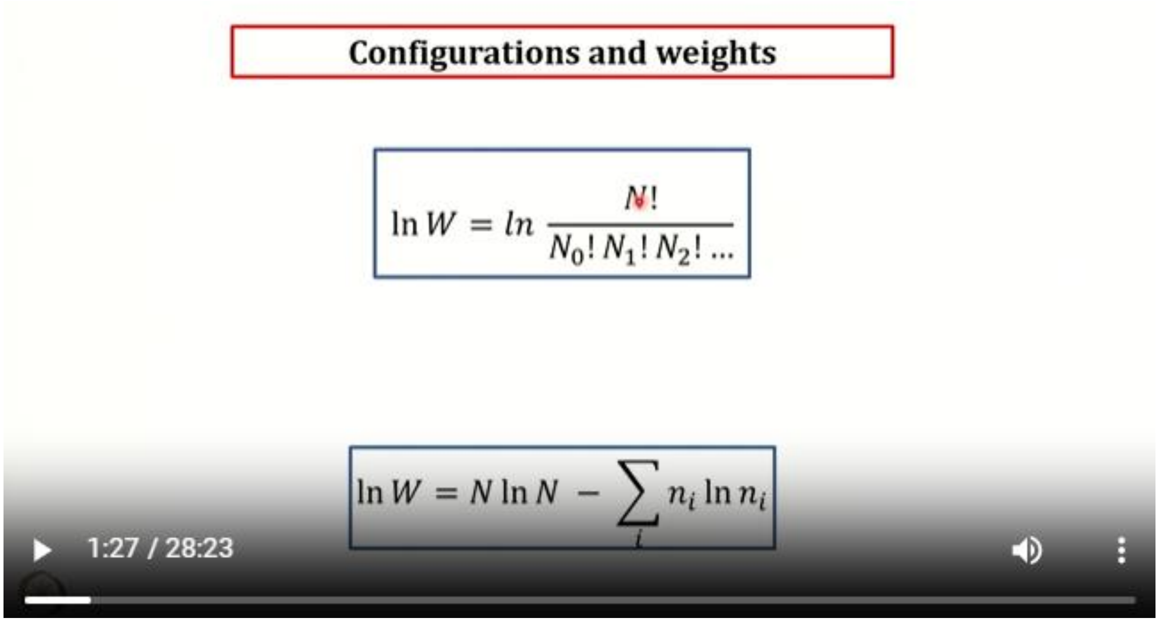
Lecture - 03

Welcome back to the next lecture of Statistical Thermodynamics. In the previous lecture, We talked about very basics of, you know, what is required and what we are considering to derive the various formulae, what are the various postulate kind of things that we need to keep in mind before we go to the next steps. Yesterday, we talked about the weight of a configuration. We sort of derived a formula that if there are various instantaneous configurations, then how to calculate the weight of a configuration. So, today we will further discuss on that. Yesterday, we talked about this formula that in order to calculate weight of a configuration, W is equal to n factorial over n_0 factorial, n_1 factorial, n_2 factorial, etcetera.



Configurations and weights

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

$$\ln W = N \ln N - \sum_i n_i \ln n_i$$

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

But if you notice here, here I have written logarithm of W. My aim is today to start with the definition of statistical weight or weight of a configuration to arrive at an equation that is

$$\ln W = N \ln N - \sum_i n_i \ln n_i$$

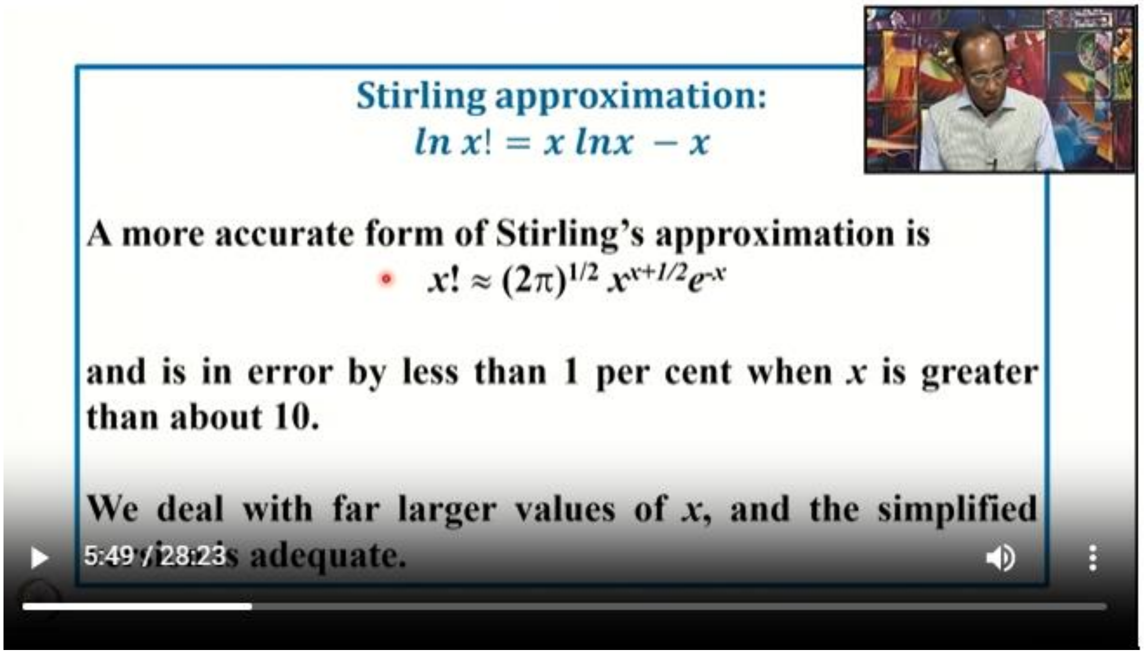
. Now, obviously, a question may come in the mind that why are we working with log W. Let me give some sort of explanation in terms of some concepts in chemical thermodynamics.

You remember that when we used to talk about internal energy, we used to talk about that internal energy is a function of temperature and volume. And then why did we used to, you know, usually take internal energy as a function of temperature and volume where p, v, t are related with each other. We can also take internal energy as a function of temperature and pressure. We can also take internal energy as a function of pressure and volume. But why did we used to take? Because if I write dU for here, this will be equal to del U by del t at constant V dt plus del U del V at constant T dV.

I chose internal energy as a function of temperature and volume. So, that if there is a small change, I can write dU is equal to del U del t at constant V dt plus del U del V at constant T dV. Now, if you carefully examine this, this dU is connected to del U del t at constant V, which is nothing but heat capacity at constant volume. And the second derivative, which is pi t, both these derivatives are experimentally measurable. So, the advantage of choosing internal energy as a function of temperature and volume is that you can connect these changes in internal energy, that is dU with exponential experimentally measurable quantities.

So, naturally you know one may have this question in mind that we can also get the same equation if we express internal energy as a function of temperature and pressure. Answer is yes, but then the path will be lengthier. Therefore, to act smart, we can choose internal energy as a function of something, which allows us to connect any changes with the experimentally measurable quantities comfortably, conveniently and easily. And that is the reason, instead of W, we will like to work on log W and then develop further equations based on this. So, before I move ahead, I will be using Stirling approximation in developing or taking the theory ahead or derivation ahead.

What is Stirling approximation? Stirling approximation is



Stirling approximation:

$$\ln x! = x \ln x - x$$

A more accurate form of Stirling's approximation is

- $x! \approx (2\pi)^{1/2} x^{x+1/2} e^{-x}$

and is in error by less than 1 per cent when x is greater than about 10.

We deal with far larger values of x, and the simplified [illegible] is adequate.

$$\ln x! = x \ln x - x$$

This is the form of Stirling approximation I am going to use. Actually, a more accurate form of Stirling approximation is given here.

$$x! \approx (2\pi)^{1/2} x^{x+1/2} e^{-x}$$

This is a more accurate form of Stirling approximation.

But when x is very large, then the error introduced is less than 1 percent if we use this upper formula, that is, log x factorial is equal to x log x minus x. And that is why you use the term approximation. It is not exact. It is an approximation. And if the value of x is very high, see what is written over here.

We deal with far larger values of x and the simplified version is adequate. We are talking in terms of n, total number of particles. So, we are talking about n. Remember, total number of particles or total number of molecules in 1 mole is equal to Avogadro constant 6.023 into 10 raise to the power 23.

And that is why we say when x is equal to very large number, this Stirling approximation can be used which will introduce error at the most 1 percent. So, keep this in mind and let us proceed further. So, we know that W is equal to n factorial divided by n_0 factorial, n_1 factorial, n_2 factorial, etcetera, etcetera, etcetera. Discussed that if we take a logarithmic form of this, then the derivations will become a little easier. So, let us take the logarithmic form.

Log W is going to be log W is equal to log n factorial. See, I am taking only the natural log minus log n_0 factorial, n_1 factorial, n_2 factorial, so on, so on. Let us move to the next step log W is equal to log n factorial minus this is log a, b, c, etcetera, log a into b into c into d which is equal to log n 0 factorial plus log n_1 factorial plus log n_2 factorial and we can keep going Another way of writing can be log W is equal to log n factorial minus summation i, log n_i factorial. I have captured everything into this summation. Now remember n is very large.

You know, if we talk about 1 mole, it is 6.023 into 10 to the power 23. If n is large, let us use Stirling approximation and we will get an approximate result. So, what do we have now? We have log W is equal to let us use Stirling approximation log n factorial is equal to n log n minus n minus summation i. Here, I will use n_i log n_i minus n_i. Let us go to the next step. Log W is equal to n log n minus n minus summation i n_i log n_i plus summation i n_i. Remember that n total number of particles, total number of molecules is summation in_i. That is the total number of particles or total number of molecules, you know, you sum up in each state. This means that this n and this n can be canceled You cancel these.

What we have. we have log W is equal to n log n minus summation i n_i log n_i. This expression I am going to use now in future for further derivation. So, what we have done? We have, instead of W, we decided to work on log W. The reason for working on log W, I just discussed that if we work on log W, we will come up with some expression that can easily be transformed into the desired result.

That is the reason. So, what we have now is log W is equal to n log n minus summation n_i log n_i. All right. So, remember in the previous lecture, we talked about, Instantaneous configuration, let me write 1 as n 0 0 etcetera. The second instantaneous configuration we talked about was n minus 2, 2, 0, 0, 0 etc. The first one This instantaneous configuration can be achieved only in one way where all the particles or all the molecules are in the ground state.

We also discussed yesterday that the second one n minus 2, 2, 0, 0, this can be achieved in more than one way. Precisely, we derived in the previous lecture, it is half into n into n minus 1 number of ways. So, if the system were to choose between these two, obviously the system would like to stay or remain in this instantaneous configuration because this is the one which can be achieved in more number of ways. So, I have talked about these two only. There can be more instantaneous configuration for example, n minus 5 2 3 0 0.

There can be many other instantaneous configurations under given conditions and each instantaneous configuration for each instantaneous configuration, you can calculate the weight of a configuration. We have discussed the formula w is equal to n factorial over n_0 factorial n_1 factorial, etcetera, etcetera. You can use and one can calculate the weight of a configuration w. This weight is going to be different for different configurations. There will be at least one configuration where the weight of that configuration is going to be very high.

So, the system is more likely to show the properties of that configuration. That means the system would like to stay in that configuration which has the maximum weight. So, therefore how do we go about finding that configuration which has the maximum weight? We know w. We have talked about w and we want to find out a configuration which has a maximum weight. Just like in mathematics, you know how to find the maxima and minima.

If we have w, we want to find the maxima. That means set the derivative equal to 0 d w equal to 0. So, therefore our approach is going to be that we will set w equal to 0, but as I will show bit later that we will not directly work through w. We may work through log w and I will be going to discuss that now ahead. So, how do we now go about finding out that maximum w? Let us look at first before we move ahead.

Let us look at this configuration and this configuration. Let us first see whether the total energy of these two configurations is same. The total energy of this configuration, all the molecules are in ground state E_0 and we set E_0 is equal to 0. That means the total energy here in this case is 0. Here, this is going to be n minus 2 into whatever is the energy E_0 plus 2 times E_1 first excited state.

This is 0. This is non-zero. That means that total energy requirement is being violated here. Only those instantaneous configurations will be permitted in which the total energy is same, total energy of the system is the same. That means many instantaneous configurations will anyway be ruled out. So, therefore, what are the constraints? We need to now talk about the constraints. Let us again take a look at these two configurations. In the first one, the total number of particles or molecules is n. In the second one, the total number of particles or the total number of molecules is n minus 2 plus 2 which is n. the total number of particles has to remain same. That means when some of the molecules are excited to upper state, obviously, if the upper states are getting populated, the lower states will have some number of molecules less. However, the total number of molecules has to remain constant.

So, therefore, let us write the first constraint that is summation in_i is equal to n. The total number of molecules or particles added up in all the energy states has to sum up to n. The second constraint, the total energy has to remain constant. How do we incorporate that? We incorporate that in this way. Summation i n_i E_i, this is the total energy of a given state, sum over all the states, that has to be equal to total energy of the system. So, therefore, the instantaneous configurations which do not follow any of these constraints are anyway going to be ruled out So this makes the things little easier because as we discussed that there can be several instantaneous configurations possible. and if out of those instantaneous configurations, some are left out because they do not either follow this criteria or this criteria, then remaining instantaneous configurations will have, each configuration will have some weight. And we have to search for those values of n i's, that means, we have to search for that configuration which gives maximum weight. So, as I just mentioned here, that for that maxima or minima kind of thing, we have to now set w equal to, derivative of w equal to 0. But remember that, just by giving, you know, citing that example of internal energy as a function of temperature and volume, we usually use that because that allows us to easily connect the change in internal energy with experimentally measurable quantities.

So, here instead of setting dw equal to 0, if we set dw equal to 0, then we have to set the derivative of log w equal to 0, that gives us the desired result easily. So, therefore, instead of working on w, we will work on log w and we will like to set d log w equal to 0, right. Remember that, weight of a configuration, of a configuration is equal to n factorial, n_0 factorial, n_1 factorial, n_2 factorial, etcetera. So, we have to set w equal to 0 etcetera. And from this, we arrived at a certain equation, that is log w is equal to n log n minus summation i n_i log n_i.

So, this is the equation that we have derived. And, our aim is to set the derivative of this equal to 0. So, before we move ahead to the next lecture, I would like you to keep in mind the definition of w. See, w is defined next lecture, I would like you to keep in mind the definition of w. See, w is defined in terms of total number of particle their factorial and the division by n_0 factorial, n_1 factorial, n_2 factorial, etcetera.

What are these n_0, n_1, n_2, etcetera? n_0 is the number of particles in the ground state, n_1 in the first excited state, n_2 in the second excited state, etcetera, etcetera. Keep in mind that n_1 does not depend upon n_0, n_2 does not depend upon n_0. They are all independent of each other. And, this feature. We will incorporate in the discussion that we are going to have in the next lecture. So, the take-home lesson from today's first lecture is that there are various instantaneous configurations possible.

But, all instantaneous configurations may not be acceptable because those instantaneous configurations have to follow the two constraints which are highlighted over here, this constraint and this constraint. Each instantaneous configuration is going to have some weight and we have to search for a configuration which gives you the maximum weight. So, therefore, we are going to set instead of dw, we will try to set d log w equal to 0 and develop certain equations. And, that we will discuss in the next lecture. Thank you very much. Thank you.