Fundamentals of Statistical Thermodynamics

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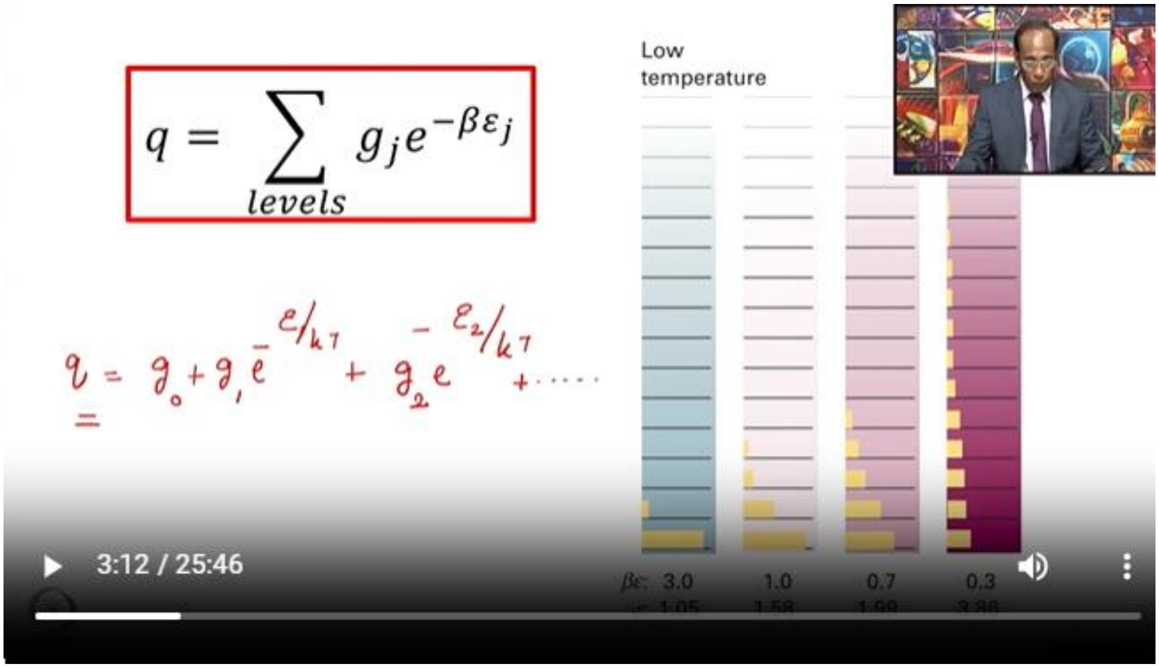
Lecture - 06

After having introduced the molecular partition function and also having discussed how to express the molecular partition function mathematically, in this lecture we will extend our discussion to a uniform ladder of energy levels. Remember in the previous lecture, we talked mostly on a system which has only two levels ground state and upper excited state. Now let us go to more number of states and first, we will talk about uniform ladder of energy levels. We have talked about how to express molecular partition function and then we also talked about what is the effect of temperature on fractional population of various states which is seen in this figure.



$$\boxed{q = \sum_{levels} g_j e^{-\beta\varepsilon_j}}$$

$$\underline{q} = g_0 + g_1 \bar{e}^{\varepsilon/kT} + g_2 e^{-\varepsilon_2/kT} + \cdots\cdots$$

See beta E is E by k T, beta is equal to 1 by k T that means when the temperature increases the beta E value is supposed to be lesser. This direction is towards increase of temperature and the bars shown here talk about the fractional population and the corresponding value of molecular partition function.

As the temperature increases the value of molecular partition function also increases and which is reflected in the form of fractional populations of various states. As the temperature increases the population of various states also increases and the value of molecular partition function also increases. Okay. So I don't mind once again writing that

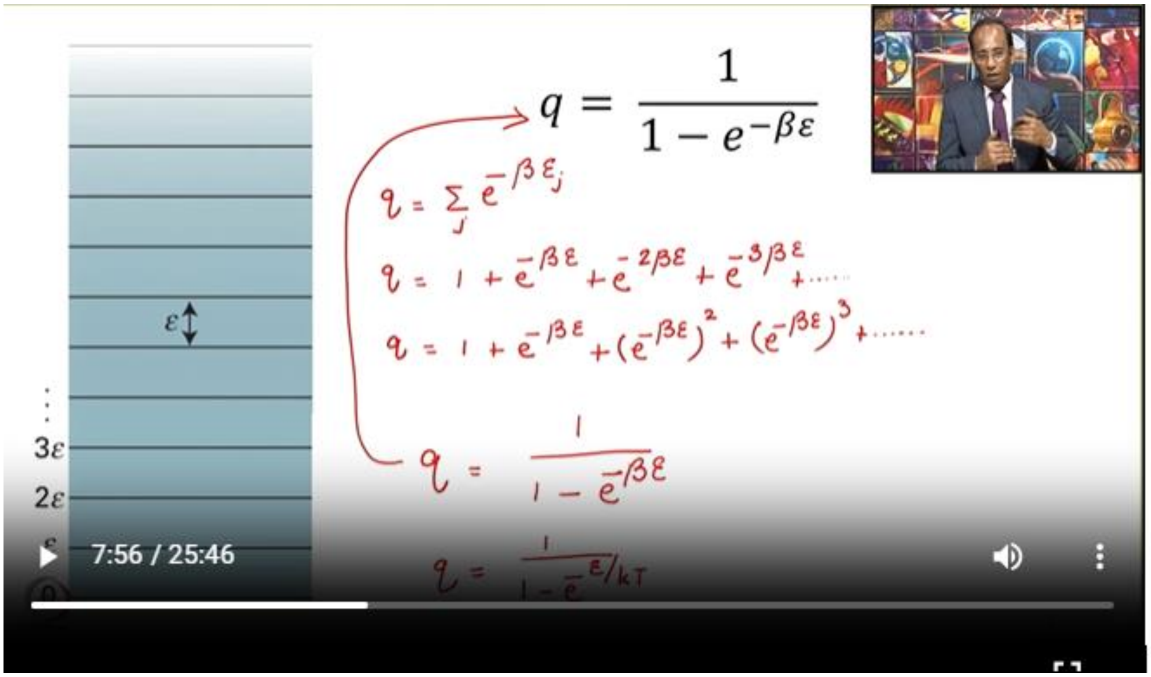
$$q = \sum_{levels} g_j e^{-\beta \varepsilon_j}$$

So therefore as the temperature increases and the more and more upper states or upper levels are getting populated the value of q will start increasing.

Ok. Now let us talk about a uniform ladder of energy levels. What is a uniform ladder of energy levels? That is a set of energy levels in which the spacing between the adjacent energy levels or states is same. This is E or epsilon whatever way you call. So each one is same maintained E or epsilon.

So ground state is 0 then first is E, second is 2 E, 3 E and so on. This is a uniform ladder of energy level. An example is a harmonic oscillator when you talk about vibrational energy levels considering harmonic oscillator let us say for a diatomic molecules and that will have the same spectrum of energy levels. That is a harmonic oscillator will be having energy levels in the form of uniform ladder that is 0, second is E, third is 2 E, fourth is 3 E etcetera etcetera etcetera. We are going to discuss how to obtain an expression for molecular partition function for a uniform ladder of energy levels and then how does the population of each state changes when the temperature is varied
We will show that the expression that we will get for the partition function for a uniform ladder of energy level is going to be 1 over 1 plus exponential minus beta. Let us see how do we get this. We start with our description of q as J exponential minus beta $E_{J.}$ Why I am not writing g_J because you notice here that each state is non-degenerate over here. So each g value is equal to 1.

So I am not including over here.



$$q = \frac{1}{1 - e^{-\beta\varepsilon}}$$

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

$$q = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} + \ldots$$

$$q = 1 + e^{-\beta\varepsilon} + (e^{-\beta\varepsilon})^2 + (e^{-\beta\varepsilon})^3 + \ldots$$

$$q = \frac{1}{1 - e^{-\beta\varepsilon}}$$

$$q = \frac{1}{1 - e^{-\varepsilon/kT}}$$

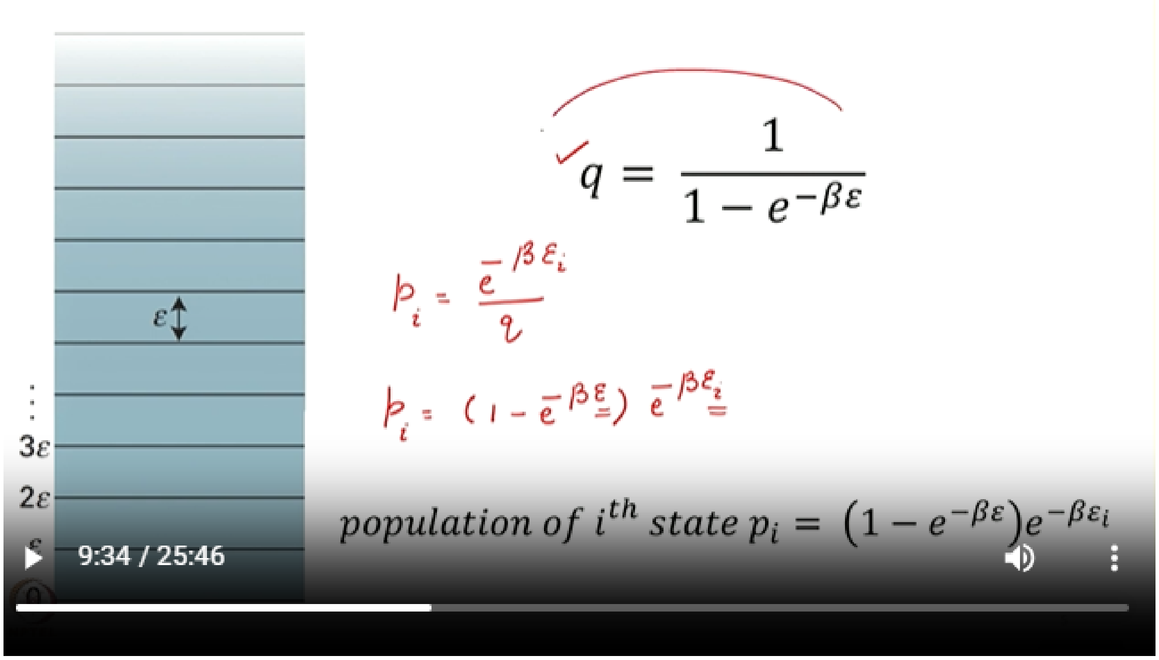
So what is then q is equal to first one E 0 1 plus second one is E exponential minus beta E, third one is exponential minus 2 beta E because it is 2 E, third one is exponential minus 3 beta E and then more and more

$$q = \frac{1}{1 - e^{-\beta\varepsilon}}$$

If you carefully examine this expression, it is like 1 plus X plus X square plus X cube. I repeat it is like 1 plus X plus X square plus X cube plus so on.

It is a geometrical progression and you know that the sum of a GP 1 plus X plus X square plus X cube plus so on sum is 1 over 1 minus X. So therefore I can write the sum over here. It is going to be q is equal to 1 over 1 minus X. X it is a common factor which is minus beta E and this is what I had written in the beginning or I can write this in this form q is equal to 1 over 1 minus exponential minus E upon K T. So therefore for a harmonic oscillator in which the various energy states are like a uniform ladder of energy levels, the partition function is given by this expression.

We will use this result later on when we will talk about the vibrational contribution to the molecular partition function. For the time being, let us keep this expression for molecular partition function in mind. Let us move ahead.



$$q = \frac{1}{1 - e^{-\beta\varepsilon}}$$

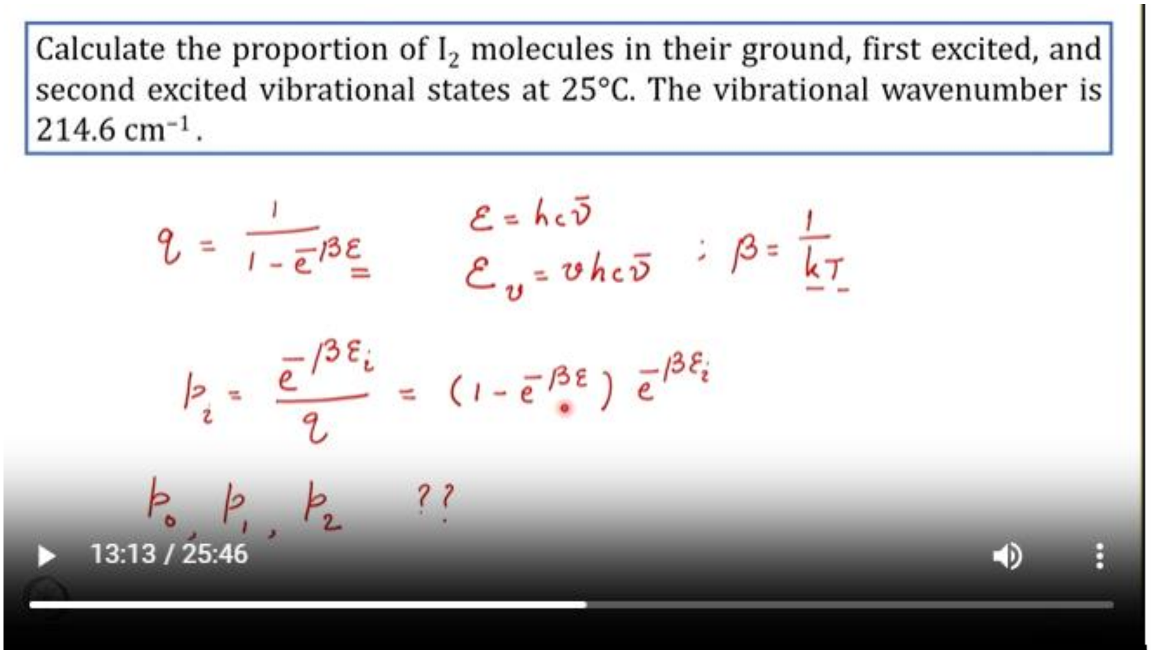
$$p_i = \frac{e^{-\beta\varepsilon_i}}{q}$$

$$p_i = (1 - e^{-\beta\varepsilon})\, e^{-\beta\varepsilon_i}$$

population of i^{th} state $p_i = (1 - e^{-\beta\varepsilon})e^{-\beta\varepsilon_i}$

So we just talked about q. This is how we can write q. The fractional population of each state is going to be exponential minus beta E I upon q. Let us substitute for q. 1 over q, 1 over q is 1 minus exponential minus beta E. This is 1 over q into exponential minus beta E I. That means if I have information about E and the energy of ith state that allows me to calculate fractional population of each state.

Remember that these expressions that we are deriving. For example, this expression that we have derived is for a uniform ladder of energy levels. These expressions are going to be different depending upon the system under consideration. Let us talk about calculation of the proportion of iodine molecules in their ground first excited and second excited vibrational states at 25 degrees centigrade. The vibrational wave number is given to us. What we have to calculate is the proportion of iodine molecules in the ground state, first excited state, second excited vibrational states at 25 degree centigrade.



Calculate the proportion of I_2 molecules in their ground, first excited, and second excited vibrational states at 25°C. The vibrational wavenumber is 214.6 cm^{-1}.

$$q = \frac{1}{1 - e^{-\beta\varepsilon}} \qquad \varepsilon = hc\bar{\nu}$$

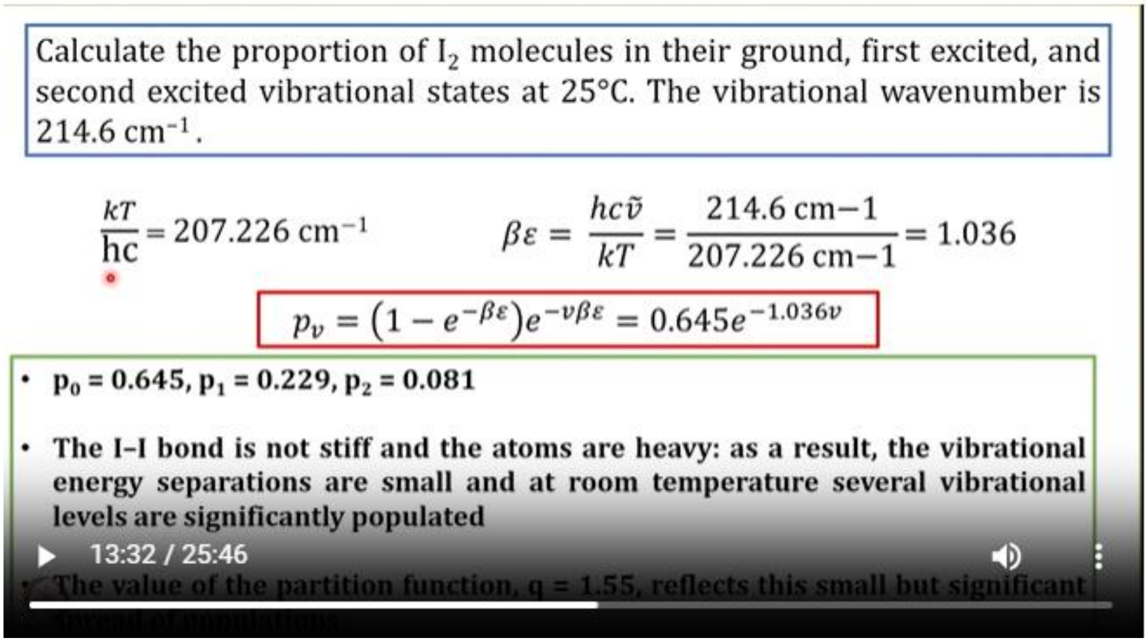
$$\varepsilon_v = v hc\bar{\nu} \quad ; \quad \beta = \frac{1}{kT}$$

$$p_i = \frac{e^{-\beta\varepsilon_i}}{q} = (1 - e^{-\beta\varepsilon})\, e^{-\beta\varepsilon_i}$$

p_0, p_1, p_2 ??

Proportion means we want to calculate fractional population of these molecules. So, we are going to use some approximation over here. Now please remember that in our discussion so far, we have used several approximations. The first approximation you remember was Stirling approximation and then we brought in the Lagrange's method of undetermined multipliers.

And here in this discussion, discussion of this problem, we are approximating the vibrational states for the sake of ease of calculation. We are going to approximate this as a uniform ladder of energy levels. And we remember that for a uniform ladder of energy levels, the partition function q was equal to 1 over 1 minus exponential minus beta E. We are given the energies in terms of wave number E is equal to hc nu bar, beta is equal to 1 over k T. I can write here E is equal to hc nu bar.



Calculate the proportion of I_2 molecules in their ground, first excited, and second excited vibrational states at 25°C. The vibrational wavenumber is 214.6 cm^{-1}.

$$\frac{kT}{hc} = 207.226\ cm^{-1} \qquad \beta\varepsilon = \frac{hc\tilde{\nu}}{kT} = \frac{214.6\ cm{-}1}{207.226\ cm{-}1} = 1.036$$

$$\boxed{p_v = \left(1 - e^{-\beta\varepsilon}\right)e^{-v\beta\varepsilon} = 0.645e^{-1.036v}}$$

- **$p_0 = 0.645$, $p_1 = 0.229$, $p_2 = 0.081$**
- **The I–I bond is not stiff and the atoms are heavy: as a result, the vibrational energy separations are small and at room temperature several vibrational levels are significantly populated**
- **The value of the partition function, q = 1.55, reflects this small but significant spread of populations**

Of course, if you want to write more precisely E for a vibrational number is v hc nu bar ignoring zero point energy. And we have already discussed that beta is equal to 1 over k T, k is Boltzmann constant, T is the temperature in Kelvin. And then we discussed that p_i is equal to exponential minus beta E_i upon q, which is equal to we have just derived this in the previous slide 1 over q, 1 over q is 1 minus exponetial minus beta E into exponential minus beta E i. We are interested in knowing p 0, we are interested in knowing p_1 and we are interested in knowing p_2. What are these numbers? This is what we are interested in calculating. Very easy for p_0 is energy is 0, for p_1 the energy you know it is a uniform ladder of energy levels. So, from the value of wave number, you can easily calculate E_i. We need the value of Boltzmann constant, we need the value of temperature, we need the value of Planck's constant and we need the value of c. Remember that energies can be calculated from h c nu bar, you need the value of Planck's constant, you need the value of velocity of light and you need the value of wave number. And for calculation, you need the value of Boltzmann constant.

Sometimes it becomes easy to combine all these constants at a given temperature. Let us say here 25 degree centigrade, you first convert that 25 degree centigrade into Kelvin. 25 degree centigrade is equal to 298 Kelvin and at 298 Kelvin k into T over h into c is equal to 207.226 centimeter inverse. Those who would like they can memorize this number because if you memorize this number at a given temperature that is a 25 degree centigrade then the calculations become easier.

Otherwise you will have to put the value of Boltzmann constant, you will have the put the value of Planck's constant, you will have the to put the value of velocity of light and then calculate beta e. So, k T upon h c is 207.226 centimeter inverse, beta e is equal to h c nu bar by k T. You already know k T by h c you can substitute there and wave number anyway is there in centimeter inverse. So, beta e turns out to be 1.036. And for any vibrational quantum number p v, it is equal to 1 minus exponential minus beta e into exponential minus v beta e. If you look back e v is equal to v h c nu bar or e_i is equal to v into e that is the fact being used over here that is e i is equal to v into beta e. Beta e you have already calculated 1.036 times the vibrational quantum number which will decide the value of p_0, p_1, p_2 etcetera. So therefore, when v is equal to 0 p_0 is going to be 0.645 here. When v is equal to 1 you substitute and calculate p_1 is going to be 0.229, p_2 is going to be 0.081. These are the fractional populations this is the value of n i upon n. So, what you notice here is that p_0, p_1, p_2 as the levels increase the ground state to first excited state to second excited state. The fractional population at a given temperature is decreasing, but still it is significant even if we consider this first two or first three. The occupancy fractional occupancy of ground state first excited state are significant and the second excited state can also not be ignored. We can obtain some more insights. The given example is for iodine.

Iodine has I bond. The i i bond is not stiff because the atoms are very heavy and from the knowledge of vibrational spectroscopy you can connect with that results that for this type of molecules where the bond is not stiff and atoms are heavy the vibrational energy separations are small. And at room temperature several vibrational energy levels are significantly populated. Now at this point I would like to bring in some discussion on different types of modes of motion. What are the different types of modes of motion a molecule can possess an atom can possess? Translational degree of freedom, rotational degree of freedom, vibrational degree of freedom, electronic and if there are any other. And when the temperature is increased this is the order in which the degrees of freedom or the various modes of motion become active.

For a gas molecule translational degree of freedom is always there. At room temperature rotational degree of freedom is mostly there. And then it comes in this order translational then rotational then vibrational then electronic. So for the vibrational energy levels to be populated the temperatures has to be high. The example that is being discussed over here that is iodine.

Since we talked about that iodine bond is not stiff and atoms are heavy and vibrational energy levels separations are small and even at room temperature you see several vibrational levels are significantly populated. Here when I say several that means I am talking about p0, p1, p2 and fractional population is 0.645, 0.229 and 0.081. And since pi or pv whatever way you want to express is equal to ni upon n you can always calculate the number of molecules. That is in terms of fractional population but if I know n total number of molecules we can always calculate it how many molecules will be there in the ground state, in the first excited state, in the second excited state. Now let us take a look at the

value of partition function. Partition function since here we are talking about the uniform ladder of energy levels we have already discussed that for a uniform ladder of energy level partition function is going to be 1 over 1 minus exponential minus beta E. We know the value of beta 1 over kT, we know the value of E hc nu bar and therefore, we can calculate the value of molecular partition function at 25 degree centigrade. The value of partition function is 1.55. The question is, is this value 1.55 very small or is this very large? As we will see ahead that the value of partition function for translational degree of freedom is going to be very very high. For rotational degree of freedom also the value of partition function is relatively large. For vibrational contribution to partition function generally at room temperature the value is nearly 1. Here in this special case of iodine for the reasons that we already discussed the value of molecular partition function which is 1.55 here although it is a small number it reflects a small value, but there is a significant spread of populations. Why am I saying the significant spread of populations? Because if you look at the values of p_0, p_1, p_2 in fact, if you calculate p_3 also you will see there is a significant spread of populations. So, what we have covered in today's lecture is how to write expressions for molecular partition function for a uniform ladder of energy levels. These are very simple examples because the solutions can be easily achieved. We could easily derive an expression for a uniform ladder of energy levels and we can easily calculate the fractional population of each energy state.
By taking the example of iodine molecule and by using the harmonic oscillator approximation we could calculate the partition function and the fractional occupancy of in fact, we can calculate for many vibrational states which definitely the population is going to depend upon temperature. With this basic background knowledge of molecular partition function the way how to express molecular partition function for simple systems we will now start discussing the partition functions for different modes of motion like translational, rotational, vibrational, electronic, etcetera and those we are going to discuss in the next lecture onwards.

Thank you very much.