Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

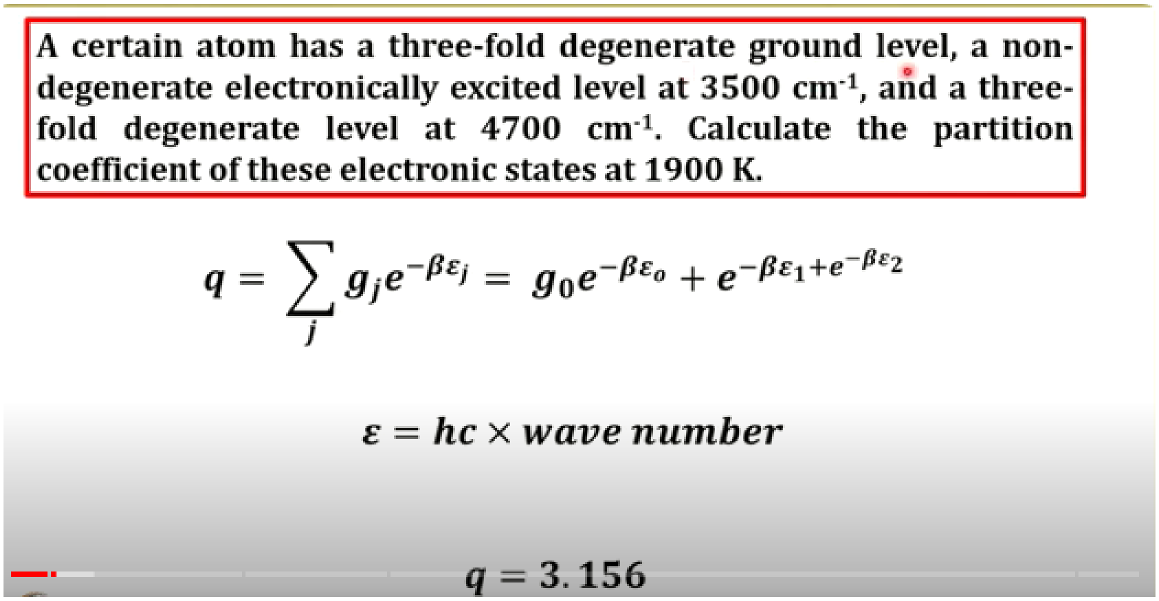
Indian Institute of Technology, Bombay

Lecture – 11

The Internal Energy

Welcome back to the next lecture on internal energy. Today, we are going to connect the partition function with a thermodynamic quantity, which is very important the internal energy. But before I switch over to internal energy, remember that in the previous two lectures, we have solved some numerical problems and due to the shortage of time in the previous lecture I could not cover one numerical problem that I would like to do now. And after that I will start connecting partition function with internal energy. Let us try to look at this problem. A certain atom has a threefold degenerate ground level a non-degenerate electronically excited level at 3500 centimeter inverse and a threefold degenerate level at 4700 centimeter inverse.

Refer Slide Time: 1:08



A certain atom has a three-fold degenerate ground level, a non-degenerate electronically excited level at 3500 cm^{-1}, and a three-fold degenerate level at 4700 cm^{-1}. Calculate the partition coefficient of these electronic states at 1900 K.

$$q = \sum_j g_j e^{-\beta\varepsilon_j} = g_0 e^{-\beta\varepsilon_o} + e^{-\beta\varepsilon_1 + e^{-\beta\varepsilon_2}}$$

$$\varepsilon = hc \times wave\ number$$

$$q = 3.156$$

What is the question? The question is to calculate the partition function of these electronic states at 1900 Kelvin. Now, if you carefully read the statement, it talks about electronically excited levels. You remember that when we were discussing partition function, and different contributions to partition function, we were talking about translational contribution, then rotational, vibrational, and electronic will come in. The translational contribution we have already discussed.

Even in the order of energy, energy separations, this is first translation, then rotational, then vibrational, then electronic. That means even when we talk about the temperature effect, you keep on increasing the temperature, translational contribution for a gas is always there and then rotation will come in and as you keep on increasing the temperature, vibrational contribution and then electronic contributions can come in. So, this particular numerical problem talks about an atom having a threefold degenerate ground level and then you have a non-degenerate electronically excited level and then you have a threefold degenerate next level. So, in a sense even right now we are talking about electronic contribution to the overall partition function. We will start with the definition of partition function.

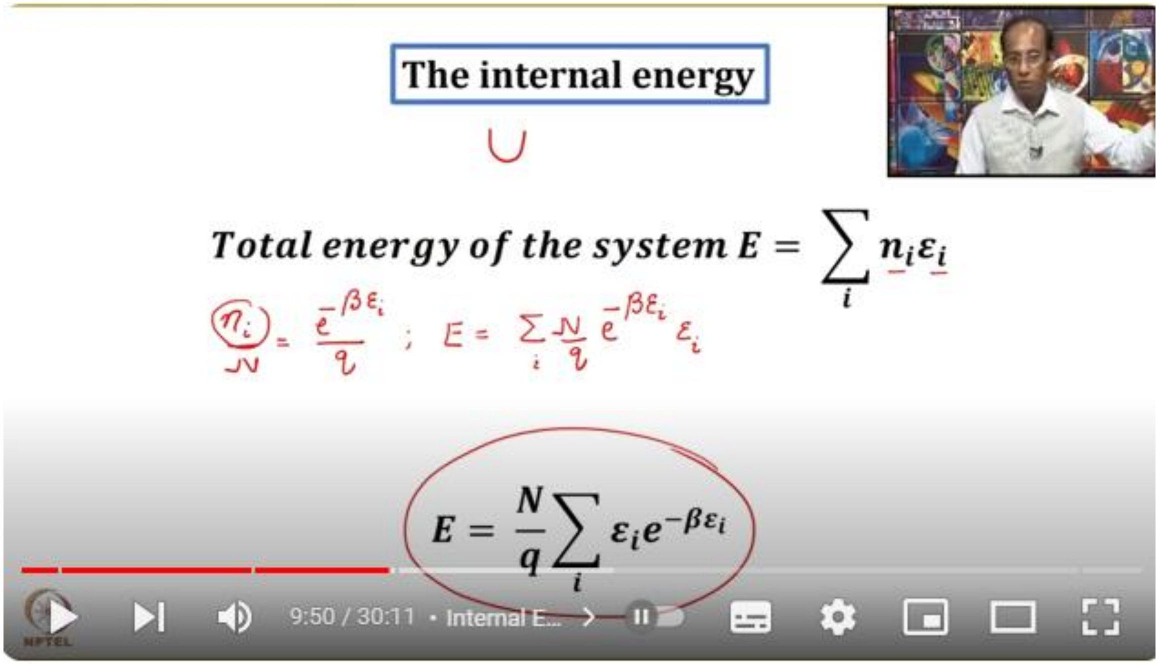
The partition function q is equal to summation j g_j exponential minus β e_j. There are only three levels which we need to consider. What are those? We will consider this. This is equal to when you open this, g_0 that is the first one plus g_1 exponential minus β e_1 plus g_2 exponential minus βe_2. Ignore this.You read this. There is some mistake over there and you are given the values of the degeneracy of the ground state, first excited state, second excited state. The ground state is threefold degenerate. So, g_0 is equal to 3 and then there is a non-degenerate first excited state and a threefold degenerate another level. So, that means your q is going to be there is threefold ground state degeneracy plus non-degenerate g_1 is equal to 1 exponential minus βe_1 plus 3 times exponential minus βe_2 and energy is equal to h c nu bar.

The wave numbers are given. So, you can easily calculate the values of e by using Planck's constant, speed of light and wave number and once you put in those numbers, the value of partition function comes out to 3.156. Now obviously, when you compare this with translational contribution, your translational partition function, remember that for a gas, the translational partition function for a molecule which is free to move in three dimension was of the order of 10 raise to the power 25, 10 raise to the power 26, but if you look at here, the electronic contribution is not very high, 3.156 even at a temperature as high as 1900 kelvin.

So, in any case, we are going to discuss the electronic partition function again after we have discussed the rotational vibrational contribution, but here it is just a demonstration of how to expand this expression for the partition function and consider the energy levels which are available. Now, let us start discussing about a very important thermodynamic quantity, internal energy. We have earlier discussed what is internal energy. The total energy added up in all the forms is called the internal energy. Whatever system we are considering, translational plus rotational plus vibrational plus electronic plus whatever other forms of energies may be there, you add up all the energies in all the forms that is equal to the internal energy.

The symbol used for internal energy is u. To derive internal energy, let us start with the definition of total energy of the system. The total energy of a system is equal to summation i n_i e_i. This we have earlier discussed. Now, from this, I want to connect this expression with partition function.

Refer Slide Time:9.50



The internal energy

U

Total energy of the system $E = \sum_i \underline{n_i}\underline{\varepsilon_i}$

$\frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{q}$; $E = \sum_i \frac{N}{q} e^{-\beta\varepsilon_i} \varepsilon_i$

$$E = \frac{N}{q}\sum_i \varepsilon_i e^{-\beta\varepsilon_i}$$

That is my goal. So, let us think of the ways to connect this expression with the molecular partition function. A simple way let us discuss. We have derived this expression that n i upon n is equal to exponential minus β e_i upon q fractional population Boltzmann distribution and from here, I can write an expression for n_i into energy. So, what do I get? Now, let us substitute into energy.

Energy is equal to summation i. In place of n_i, I will write n upon q exponential minus β e_i and I have another e_i here. I have substituted for n_i by using this Boltzmann distribution. So, n i, this n i is equal to n upon q exponential minus beta e. That is what I have substituted over here and e i is remaining over there.

So, now, n which is the total number, q is the partition function. These can come out of this summation and you get this expression. e is equal to n by q summation i e i exponential minus beta e i. So, at least we have reached one step. We have connected the total energy of the system with the molecular partition function, but still what we have is this summation term.

How to account for this summation term? How to calculate the values corresponding to specific values of e i's? Can we further work on it to make it simpler? Yes, we can do it. Let us work on that. So, what we had is that e is equal to n upon q e_i exponential minus beta e i. We want to simplify this summation term. How do we simplify this summation term?Let us consider the derivative of only exponential βe. Let us consider this derivative, d β of exponential minus beta e. Let us consider this. What do we get? It is d d beta of exponential minus beta e i is equal to exponential minus β e_i and we have minus e i and that is what you have over here. All right. So now, you see we have an expression for e_i into exponential minus βe_i.

We can substitute over here. Once you substitute over here, the negative sign is there. So, substitution over there is equal to this negative sign comes from there, n over q, summation i, d d β of exponential β i because that is what exponential of minus beta e i into e i is, d d beta of exponential minus beta e i. So, these operators I can interchange these. Mathematically that is allowed.

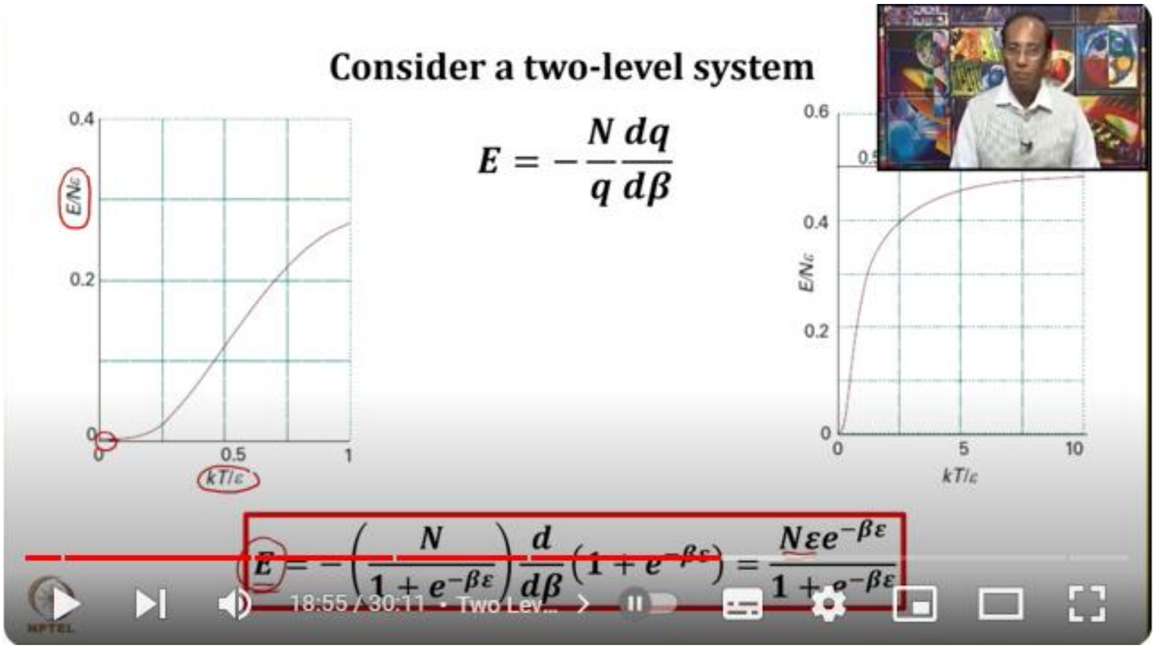
Minus n by q, d d β of summation i exponential minus beta e i. You recognize that this summation, summation i exponential minus beta e i is nothing but partition function. So, the expression that we get is minus n by q, d q by d beta. So, we have now an expression for the total energy which is connected with the molecular partition function and we need to take the derivative of the molecular partition function concerning β. Please note here that beta is equal to 1 over k T. So, therefore, different books may express this in terms of temperature also. So, do not get confused when you see this in terms of d q by d T. β is also a temperature, but there is a Boltzmann constant involved in that. Okay. So, as of now we have an expression for the total energy, e is what? e is total energy. Let us now apply this expression to a two-level system. From the beginning, we have taken many times the example of a two-level system or a three-level system. Let us talk about a two level system. So, what is a two-level system? You have a ground state and you have first excited state.

This is 0 and this is e. The energy is given by minus n by q, d q by d β. So, what we need is to write an expression for the molecular partition function. Let us write q is equal to 1 plus exponential minus beta e. This is the expression for q for this two level system. q is equal to summation j i whatever you want to write, g j exponential minus beta e.

Basically we are expending this all the time. So, therefore, what is the energy, total energy? Exponential energy is equal to minus n by q, q is 1 plus exponential minus beta e into d q by d beta. This is going to be exponential minus beta e and into you have minus e. So, what do we have now? e is equal to n times e over 1 plus exponential minus beta e and also we have another term which is exponential minus beta e. So, total energy can be expressed in terms of energy separation which is this e epsilon and exponential minus beta e which includes the terms for energy and the terms for temperature.

This we are talking about a two-level system. We can plot actually from this we can plot energy as a function of temperature and then see how the energy varies when the temperature is changed. Let us take a look at this. We have derived that energy is equal to minus n by q d q by d beta and then since we talked about a level system, we also derived this expression that total energy is n e exponential minus beta e 1 plus exponential minus beta e. So, you plot e upon n_e. It is easy you know it sometimes becomes easier if you take e divided by n e then the remaining terms are in terms of temperature. It becomes easy. So, that is what is done over here. You plot e by n e versus k T by e. You can plot in fact e versus temperature also.

Refer Slide time: 18.55



Consider a two-level system

$$E = -\frac{N}{q}\frac{dq}{d\beta}$$

$$E = -\left(\frac{N}{1+e^{-\beta\varepsilon}}\right)\frac{d}{d\beta}\left(1+e^{-\beta\varepsilon}\right) = \frac{N\varepsilon e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}$$

the shape of the plot is not going to change, but only the numbers on the x-axis and y-axis may be different. So, you see when k T by e is in the range of 0 to 1, right, when the temperature is 0 then all the molecules are in the ground state. The total energy is 0. So, it starts from 0 and as the temperature increases there is a rise and eventually when the temperature becomes infinity then the value of e by n e, e by n e, you can see from here e by divided by n e is going to be 1 by 2, 0. That is what you see here. When the temperature becomes very high this e by n e starts from a value of 0 and it is approaching a value of 0.5. So, initially, the energy was 0 and where the temperature is approaching a very high number when the temperature is approaching infinity the energy divided by n e is getting half of its maximum value. Isn't it endorsing or isn't it another way of saying what we have discussed earlier that when the temperature approaches a very high number when the temperature approaches infinity then all the states are equally likely populated? Here, you know, we are talking about a two-level system and similarly, you can take a three-level system, four-level system, you can bring in degeneracy and derive various expressions. So, this is about the total energy of a system. Now, we want to talk about the internal energy. How to recover the internal energy from total energy? Again I refer to the initial lectures. We discussed that some systems, for example, oscillators may have some zero-point energy. So, therefore, if for our discussion if we set the ground state energy to be 0 then to obtain internal energy we will have to add a constant to the total energy, and that constant depends upon, you know, if it is an oscillator then it is a zero point vibrational energy.

So, now you look at the expression that to obtain internal energy to the total energy we are adding a constant and that you are referring it to u 0 and refer to the previous discussion what we just derived that total energy is equal to minus N by q dq by d β and instead of E I can write u minus u (0), left side is taken care of. Now, when you are dealing with different systems, you know, usually we keep some constraints. You remember that in chemical thermodynamics one question which is usually frequently asked is what is the criteria of spontaneity and the usual answer is that if delta G is less than 0 then the process is spontaneous, but just by saying that delta G is less than 0 the process is spontaneous that is not a complete answer. The complete answer is that delta G at constant temperature and pressure is less than equal to 0 is for a spontaneous process. Equality refers to equilibrium and less than means it is a spontaneous process.

So, you put generally the constraints and when we deal with internal energy and usually under those conditions, you know, as I said that when we are dealing with internal energy we deal with constant volume conditions. So, let us invoke here the constant volume conditions so that the expression for the internal energy becomes u is equal to u 0 minus N by Q del Q by del B at constant V. Now you note here that we are using the partial derivatives because you are keeping the volume constant and you can convert d q by q into d into d log Q that is the new expression or an alternate form of the expression can be u is equal to u 0 minus N del log q by del B at constant volume. So, what we have done? Now we have obtained an expression for the internal energy which connects internal energy directly with the molecular partition function. You can use any of these two equations. The information required is N the total number of molecules and secondly the molecular partition function. The molecular partition function is translational, rotational, vibrational, electronic whatever it is. So to determine the value of internal energy concerning internal energy at T equal to 0, we need information on N, and we need information on Q. So, obviously, you know a question can come that in chemical thermodynamics when we were asked how can you experimentally determine the value of change in internal energy. Absolute internal energy determination we were not talking in chemical thermodynamics. We used to talk about how to experimentally measure the value of change in internal energy. Remember delta U, delta U was equal to heat supplied or heat taken out under constant volume conditions. Therefore, experimental determination of change in internal energy requires measurement of heat supplied to the system or taken away from the system under constant volume conditions, and the calorimeter that is used for the determination of delta U is called a bomb calorimeter. Right, but that is the experimental determination of change in internal energy. Here we are talking about the determination of internal energy. Of course, here also we are keeping a reference which is U0. We need the value of q and q, what is q? q is equal to summation j g_j exponential minus beta Ej. So, if you are using the concepts of statistical thermodynamics and we are asked how we will determine the value of internal energy concerning U (0) concerning t equal to 0, this is the expression for partition function we need to consider. Therefore, the information that we require is the value on degeneracy and temperature because beta talks in terms of temperature and the energy levels information on the energy state energy levels. And how do we get information about energy states and energy levels? By using appropriate spectroscopy. So, that is what I was saying in the beginning that experimental determination of many thermodynamic signatures like internal energy delta U, delta G, delta H, Cp it requires calorimetry. And if you want to apply the concepts of statistical thermodynamics, what we are showing here is that the same thermodynamic quantities, currently we are talking about internal energy can be determined spectroscopically because the information on degeneracy and energy levels will come from spectroscopic measurements. So far, after having deriving an expression for the molecular partition function, we have now connected the molecular partition function with one very important thermodynamic quantity the internal energy. I am again and again reemphasizing on the meaning of internal energy. It is the total energy of the system added up in all the forms.

Also if you look at you know this expression, we are adding to the total energy, we are adding the zero point energy also or some constant which corresponds to zero point energy. We will discuss further on internal energy in the next lecture. We are going to now obtain an expression for the other constant which was used in Lagrange's method of undetermined multipliers, but that we will do in the next lecture. Thank you very much. Thank you.