Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

Indian Institute of Technology, Bombay

Lecture: 49

Contributions to equilibrium constant

Welcome back to the next lecture on Statistical Thermodynamics. We have been talking about equilibrium constant and by now we have developed some relations between equilibrium constant and molecular partition function. And based on those derived equations we have also solved some numerical problems. Minimal problems starting from simple dissociation of a diatomic gas to a little complex systems in which the reactants and products are a combination of linear or non-linear rotors. Please remember that whenever you are dealing with such systems it is very important to look at the stoichiometry of the reaction and make appropriate representations there in the equation. Equilibrium constant is connected to change in standard molar reaction Gibbs free energy change.

And $\Delta G°$ when we write equal to minus RT log K remember that $\Delta G°$ is also equal to $\Delta H°$ minus T $\Delta S°$. So therefore, there are two contributions one is enthalpy change and the other is entropy change. And you know from your concepts of chemical thermodynamics that both the enthalpy change and entropy change make a difference in the overall sign and value of $\Delta G°$. The overall spontaneity is decided by the sign and magnitude of $\Delta H°$ and T $\Delta S°$.

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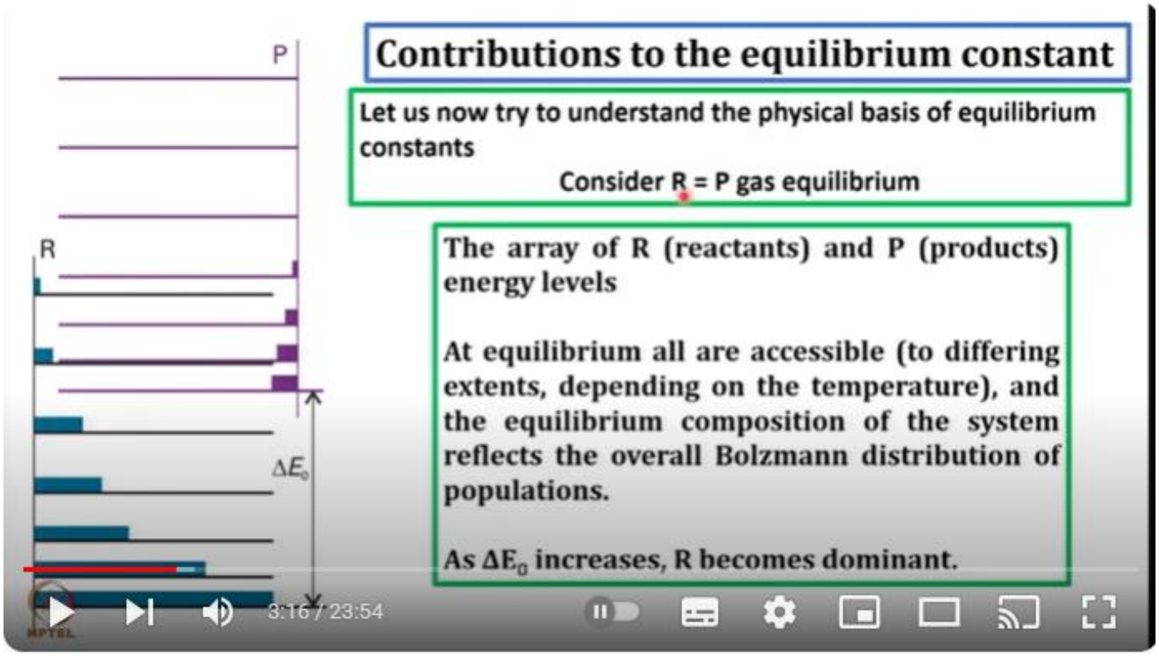

But those are the concepts that we discussed in classical in chemical thermodynamics. But when we are talking about the discussion in statistical thermodynamics today we will discuss that the same principles apply here too. We cannot just go by ΔG° both ΔH° and T ΔS° make a contribution to ΔG°. So therefore, in today's discussion we are going to talk about contributions to equilibrium constant. In order to elaborate upon that let us consider a gas phase reaction R in equilibrium with P, R stands for reactants, P stands for products.

And let us try to understand the physical basis of equilibrium constants. Now take a look at this figure this array of R which I mean by R by reactants this is an array of energy levels for reactants and this is an array for energy levels for products. And also note that there is a difference in their zero-point energy levels. The example that I am covering here includes the zero-point energy level of product higher than the zero-point energy level of reactants. So that this ΔE° is a positive number.

Now when you have this mixed array of energy levels some corresponding to reactants some corresponding to products. At equilibrium all these energy levels are accessible, but these are accessible to different extents. If you consider the system comprising of energy levels as shown here you can see the spacings in energy levels for reactants represented by blue and the spacing of energy levels for product represented in violet. This population the relative population of the state's corresponding to reactants or corresponding to products will depend upon temperature. And equilibrium composition of the system reflects the overall Boltzmann distribution of populations.

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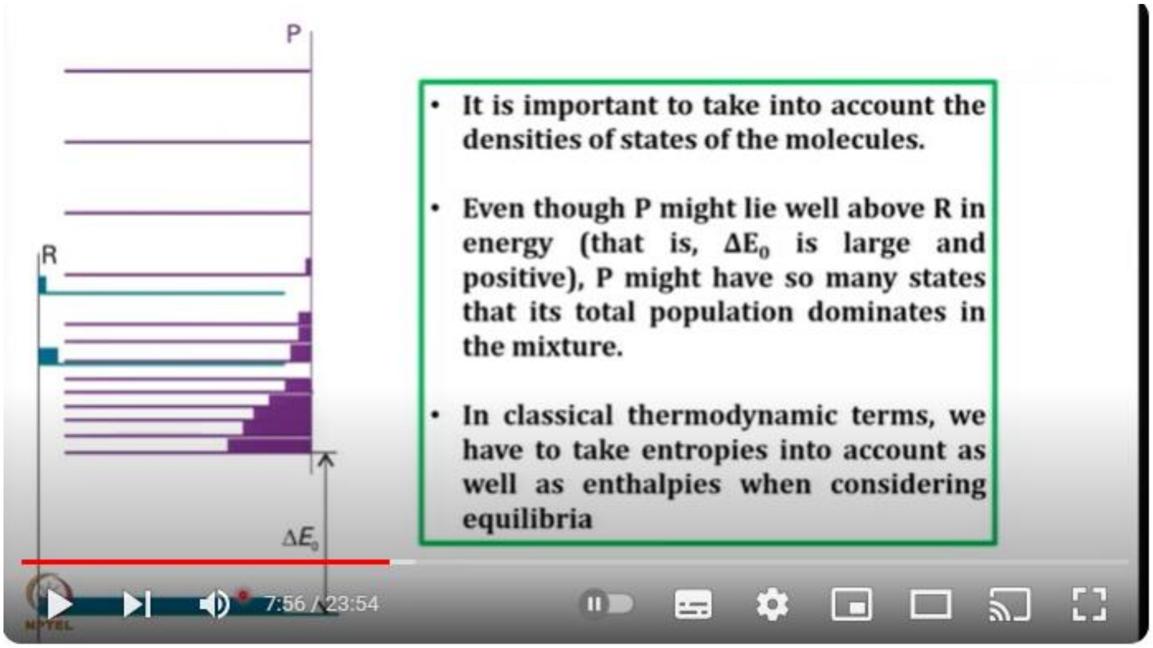

So, at a given temperature suppose there are n number of suppose there are n number of molecules. At a given temperature these n number of molecules will distribute in this way and this distribution is given by a single Boltzmann distribution. Now the relative population of reactants and products is going to depend upon temperature as well as this separation ΔE°. Similarly, as seen in this figure if ΔE° increases the population of R becomes dominant because if ΔE° increases then the population in product is going to be less and therefore, R the reactant becomes dominant under equilibrium conditions. What we are discussing over here? We are discussing the set of energy levels corresponding to reactants corresponding to products and then we have created or we have shown the difference in zero-point energies for the reactants and products.

If the product is higher than the reactant then the reaction is going to be endothermic. You can similarly show for exothermic reactions and so on. Obviously, the separation between the zero-point energy levels is going to decide whether R is going to be dominant at equilibrium or P is going to be dominant at equilibrium along with the temperature factor. Now you consider different set of energy levels. Notice that R has a big difference in energy levels.

See from zero to one this is a big difference then two etcetera. The product the density of states is high. These energy levels are very close to each other and then again becoming far separated. In this kind of arrangement, it is easy to observe that the occupation of the energy levels corresponding to product is more than the occupation of molecules in the reactants. That means, under these conditions the population of product dominates in the mixture even though P is lying above R.

Just it is dominating because you see the density of states is higher and if you count the overall population that will be more than the population of molecules in the energy states corresponding to reactants. I take you back to the previous case. Here the energy levels were similar, but you see in this kind of arrangement the population of the states for reactants is dominating at equilibrium and here the population of states at equilibrium is dominating for products at equilibrium. Now if you note the comments written over here. What the comments say? It is important to take into account the densities of the states of the molecules.

Here it is dense. Now, given though P might lie well above R. Here you can see P is lying well above R. That means, $\Delta E°$ is large and positive both large and positive. Then P might have so many states that its population dominates in the mixture. That is what we were discussing. Now look at the next comment. In classical thermodynamic terms, we have to take entropies into account as well as enthalpies when considering equilibrium. That is what I was talking to you that $\Delta G°$ which is equal to minus RT log K. I can write this also equal to $\Delta H°$ minus T $\Delta S°$ at a given temperature and that is what the comment is being made over here that in classical thermodynamic terms, we have to take into account the enthalpies as well as entropy changes.

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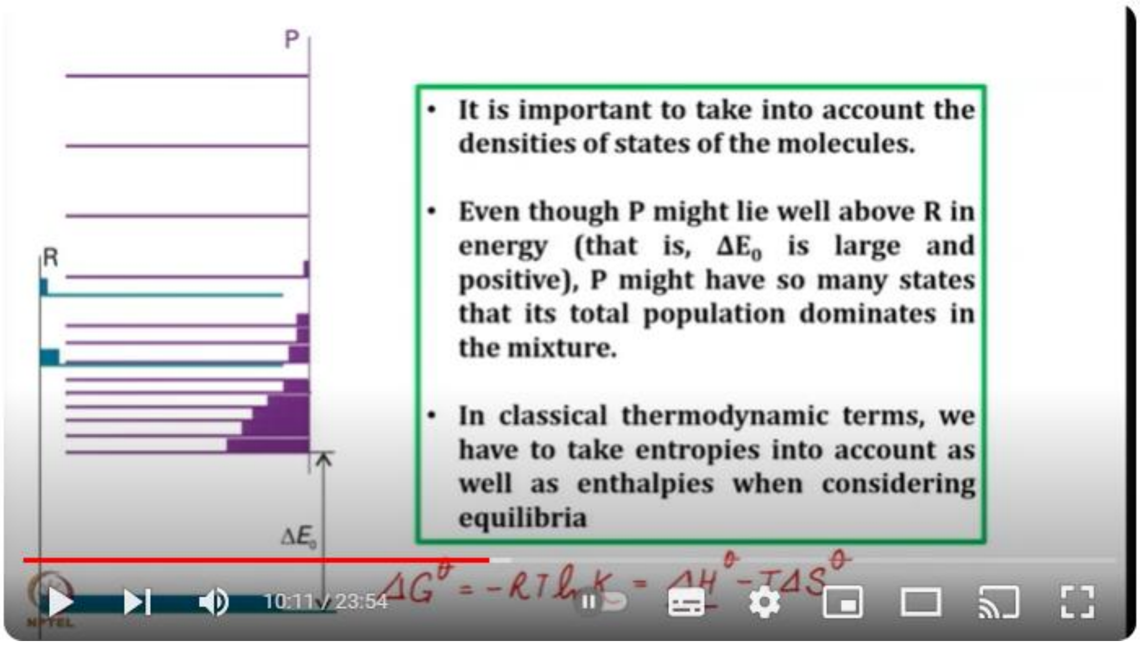

What is taking into account the enthalpies? This one and what is taking into account the entropies? This one. So therefore, the discussion is similar, but here in one diagram in one discussion, we can relate the changes in standard molar Gibbs free energy to the enthalpy change and entropy change. Now let us take the example which is shown on this slide and let us take a look at the comments. The first comment is the populations of the states are given by the Boltzmann distribution and are independent of whether any given state happens to belong to R or to P. What it means is when you have this combination of R and P, the population of these states combined states is going to be given by Boltzmann distribution.

It does not matter whether a given state belongs to reactant or belongs to product. The population is decided by the Boltzmann distribution.

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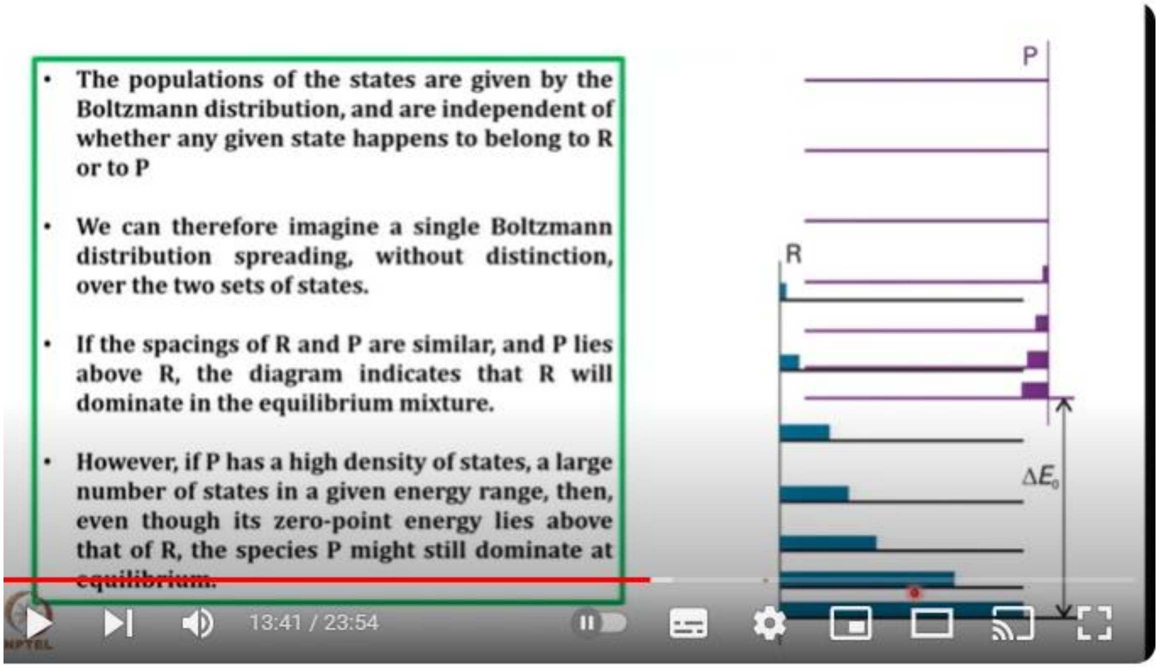

Therefore, we can consider the single Boltzmann distribution spreading without distinction over the two sets of states. Now in these two states, states corresponding to R and states corresponding to P, if you see that their density of states or their separation energy separations are similar. These spacings are similar and just a look at this diagram suggests that under the conditions of temperature, given conditions of temperature, if the distribution is like this, just by looking at you can predict that R is going to dominate at equilibrium or R will dominate in the equilibrium mixture.

And then if I replace the P by a certain product P representing very high large number of densities of states, in that case P can dominate in the mixture even though it is lying above R as discussed earlier. So, why I am talking of all these things you know and I am bringing in Boltzmann distribution also into our discussion. That means, by using Boltzmann distribution I can now quantitatively come towards the same expression that we have just discussed in couple of lectures before. And as pointed out you consider this total as single Boltzmann distribution without distinction over two states. Now, we have the reactants, we have products, we have their energy levels for the reactants and for the product.

We can calculate the number of molecules in the product and number of reactant molecules under equilibrium conditions. Once we have the numbers, this number is directly proportional to concentration. How does the number get converted into concentration?

Suppose if I have x grams of product or reactant, then I from x grams I can calculate divide by the molecular weight I can calculate the number of moles. One mole is equal to Avogadro constant number of molecules. Therefore, from the given number of moles you can calculate how many molecules will be there.

So, therefore, if I can know this ratio N_P by N_R then I can get equilibrium constant. I am going to show that this ratio is equal to q_P divided by q_R into exponential minus $_{\Delta r}$ E° by R T. Let me take you back. The reaction that we are talking here is R in equilibrium with the p and if I were to use this expression K is equal to π_j $q^{\circ}_{j,m}$ by N_A raise to the power stoichiometric number into exponential minus ΔE° by R T. This is the expression for equilibrium constant.

So, for this what I will write K is equal to partition function of product of course, standard state divided by N_A whole divided by partition function for reactants divided by N_A into exponential minus ΔE° by R T. Rearranging this I have K is equal to q_P over q_R into exponential minus $_{\Delta r}$ E° by R T. If you compare these two look at this, this is the same expression as this. So, that means, now my next step should be to find out an expression for the number of molecules product molecules and the number of reactant molecules. If I can find that expression then I can derive this expression that N_P by N_R is equal to q_P by q_R into exponential minus $_{\Delta r}$ E° by R T.

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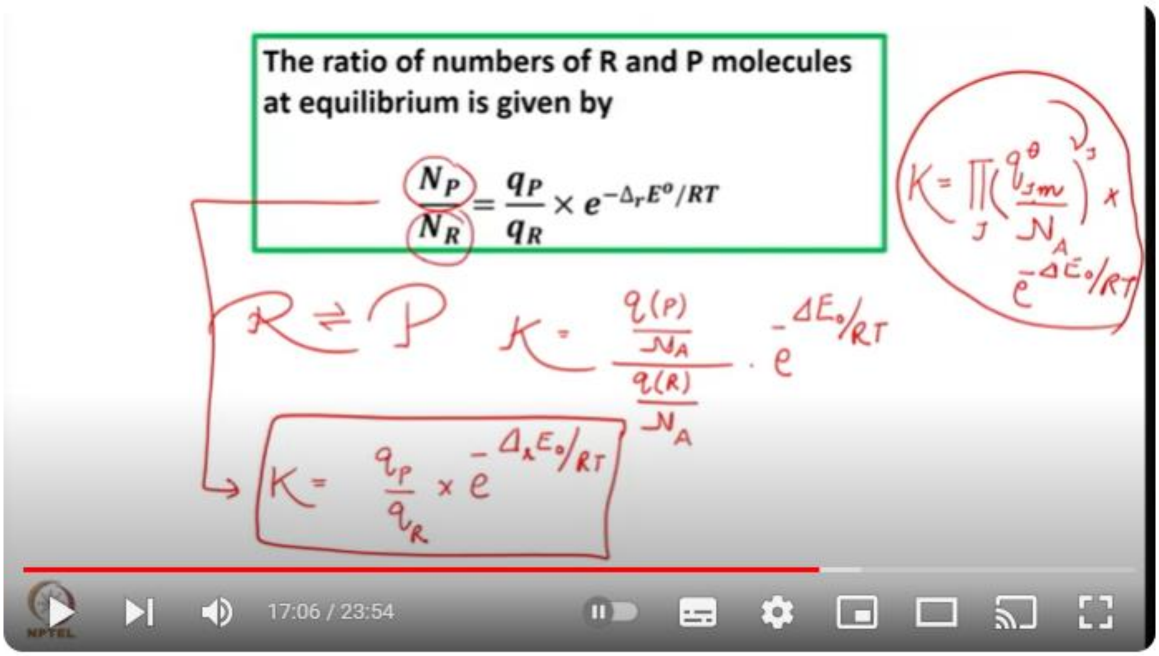

So, this is the same expression which you get by using the result that we have obtained a few lectures ago. Why N_P by N_R? Let me just reiterate again why N_P by N_R? You can take any example N_P if you just look at this distribution this talks about there are more number of molecules in the reactants and this distribution this talks about there are fewer numbers of molecules in the product. So therefore, if I can know this number of molecules in the reactant and number of molecules in the product I can the ratio of that can give me a value of equilibrium constant. How do I get now these numbers? Now, you recall that what can give you the number of molecules? Boltzmann distribution and what that Boltzmann distribution is if you remember your discussion, we had earlier N_i upon N is equal to exponential minus beta E_i upon q. This basically is the population N_i upon N is the population of the i^{th} state.

That means, from this expression I have N_i is equal to N by Q into exponential minus beta E_i where i is any i^{th} state. Now how do we get the total number? The total number of molecules will be obtained by the summation of this. You can take the sum of this N_i that is summation n_i i N_i this is N_A and if I apply this to reactants only reactants not to the product only reactants then I will get N_R.

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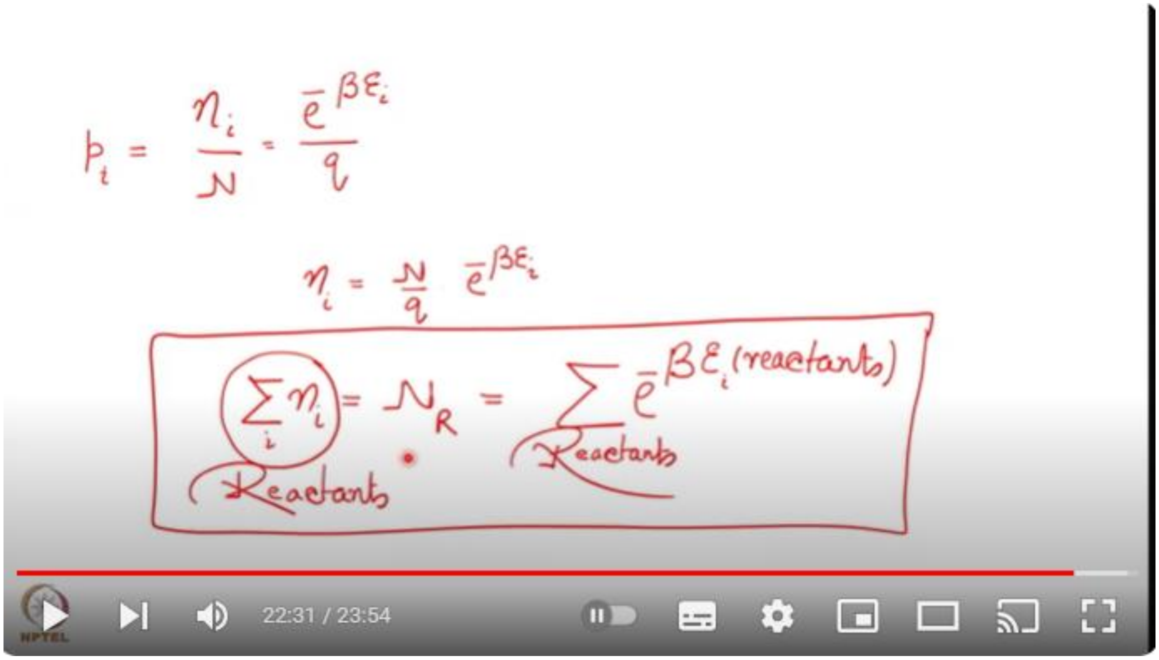

Do not get confused between this N_A and this N_R this is the total number of molecules and this is the number of molecules which are in the reactant side. Going back that means, I am talking about the number of molecules which are here in the reactant side.

Then this will be equal to summation I will only invoke reactants exponential minus beta E_i let me put i reactant. This expression is very important because this is what I need to use to obtain an expression for equilibrium constant over here. Summation N_i is equal to N corresponding to reactants and then this summation I will only apply to the reactants. Now very carefully listen when I apply this to reactants my zero-point energy is this. This is the zero-point energy of the reactants and then you have distribution and there are certain numbers of molecules and then if I write the same thing for the products then your product zero-point energy starts from here which is well above the reactants and then remaining energy levels are corresponding to this zero-point energy levels.

We will use this information when we derive the next equation, but what we have got is we have now understood how to calculate the number of reactant molecules. Once we know how to calculate the number of reactant molecules then we will know how to calculate the number of products molecules. Once we have N_P once we have N_R then take the ratio of both and we will have the expression for the equilibrium constant. The important point to note here is that our discussion has restricted to the occupation of different energy levels and we have said that this occupation or occupancy rather depends upon temperature and also depends upon $\Delta E°$ that is what is the difference between the zero-point energy levels. We have obtained an expression for N_R similarly we will obtain an expression for N_P and as I said when I talk about products the zero-point energy of the product lies above the zero-point energy of reactant and this difference we are going to consider in the derivation of the overall partition function, but that we will do in the next lecture. Thank you very much. Thank you.