Advanced Chemical Thermodynamics and Kinetics
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Lecture - 24
Introduction to Statistical Thermodynamics 03

Alright so, let us now try to find out what the rotational partition function is.

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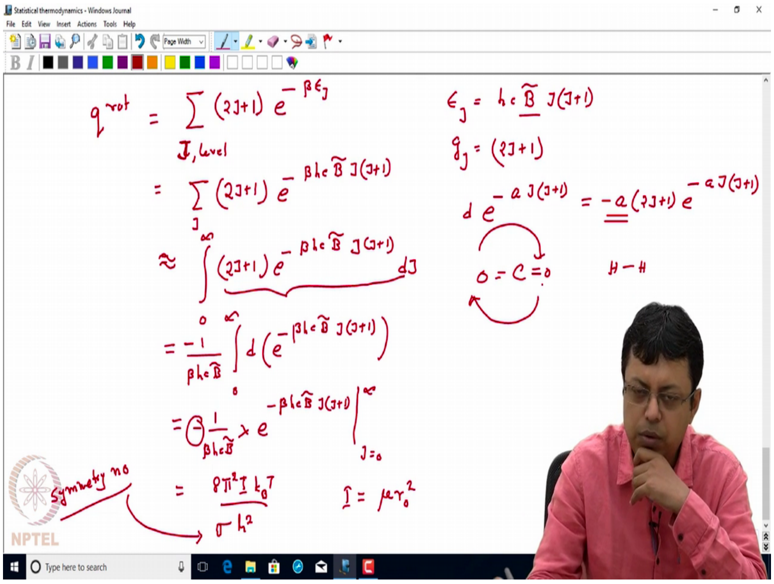

$$q^{rot} = \sum_{J,\text{level}} (2J+1)\, e^{-\beta\epsilon_J}$$

$$= \sum_{J} (2J+1)\, e^{-\beta hc\tilde{B}J(J+1)}$$

$$\approx \int_0^\infty \underbrace{(2J+1)\, e^{-\beta hc\tilde{B}J(J+1)}\, dJ}$$

$$= \frac{-1}{\beta hc\tilde{B}} \int_0^\infty d\left(e^{-\beta hc\tilde{B}J(J+1)}\right)$$

$$= \ominus \frac{1}{\beta hc\tilde{B}} \times e^{-\beta hc\tilde{B}J(J+1)}\Big|_{J=0}^{\infty}$$

$$= \frac{8\pi^2 I k_B T}{\sigma h^2}$$

$$I = \mu r_0^2$$

$$\epsilon_J = hc\underline{\tilde{B}}\,J(J+1)$$

$$g_J = (2J+1)$$

$$d\, e^{-aJ(J+1)} = \underline{\underline{-a}}\,(2J+1)\, e^{-aJ(J+1)}$$

$O=C=O$ $\quad H-H$

So, before we will just write the rotational partition function as sum over states or sum over levels, but in this case actually we will use the sum over level and notation because the rotational energy levels are say for example, if I have a rotational energy, usually the quantum number we denote as J and that we write as h c B tilde J into J plus 1 and this B tilde is called rotational constant. The way we have written it is that B tilde is expressed in units of wave numbers.

So, that is why h c into wave number even it is specifically their energy unit. Now, for any state with J quantum number, we have the energy levels are 2 J plus 1 fold degenerate. So, we can just use the other formula. It is the same formula, but just which you just have to make sure that we are taking to sum over levels e to the power minus beta epsilon J. This is capital J and then, you can just write the numbers and that will be nothing, but 2 J plus 1. So, I am summing over J now because I have changed the index and e to the power minus it will be beta h c B tilde into J into J plus 1.

Now, you see that we can actually write this thing again like before. So, as an integration because we know that the rotational energy levels compared to at room temperature, we have like a more or less continuous energy levels. So, the quantum number goes from 0 to infinity in this case and I have 2 J plus 1 e to the power of minus beta h c B tilde J into J plus 1.

Now, if you have something like say e to the power minus the inter constant, I am writing it as say a into J into J plus 1 and if I take the differential, so how that how what it will be. So, it will be basically e to the power minus a into f of x something like that differential of that. So, it will be minus a e to the power a f of x into differential of that f of x. So, together what we will get is minus a. Now, J into J plus 1 is J squared plus J. If I take the derivative, it will be nothing, but 2J plus 1 into e to the power minus a J into J plus 1. So, we see that we can actually make use of that fact and write the entire thing as a differential of e to the power minus beta h c B tilde J into J plus 1, but then we have to an extra constant minus a. So, we have to divide by that. So, you have to divide by minus of beta h c B tilde and then, this integral.

Now, this is a very straightforward integral. Now, it is integral of d x. So, it value is x. So, I have to just evaluate e to the power minus beta h c B tilde into J into J plus 1 between the limits J is 0 to J equal to infinity and I have one more constant in the form beta h c B tilde. So, the upper limit in this case e to the power minus infinity, it is 0 and the lower limit is 1 e to the power 0 is 1. So, it is 0 minus 1. So, together it will be minus 1 and now you have a minus sign here. So, it will be 1 over beta h c B tilde and we can actually write away write value of beta. You can actually look up beta is 1 over k B T, there are B tilde values and it will be I am just writing you, writing here at the final expression 8 pi square I k B T divided by h square.

Now, is moment of inertia which is mu r 0 square, where r 0 is the equilibrium bond. Suppose I am talking about a diatomic molecule which vibrates. So, if we think that it is a it does not vibrate, it is rigid in the sense that I am only considering the equilibrium bond length as if the bond length is fixed and then, it is rotating, then we can think we can say that to b r 0. So, this is the expression for rotational partition function.

Now, we have to be careful for a homo nuclear diatomic systems or systems which have a symmetry. For example, let us say if I take carbon dioxide or another homo nuclear diatomic molecule like say hydrogen, so what will happen you can see that even an 180 degree rotation will create the similar structure. So, for that we always introduce in ad hoc fashion here a number sigma which is known as the symmetry number. So, it just makes sure that do not overestimate the number of rotational states.

So, in this case c 12 or h 2 since it is a linear molecule, the symmetry number will be 2, but it can be I mean I can take some other numbers. Now, there is a reason for origin of this symmetry number and will briefly discuss that what is the reason of the origin of the symmetry number and all of you know about that normal hydrogen molecule as two nuclear isotopes.

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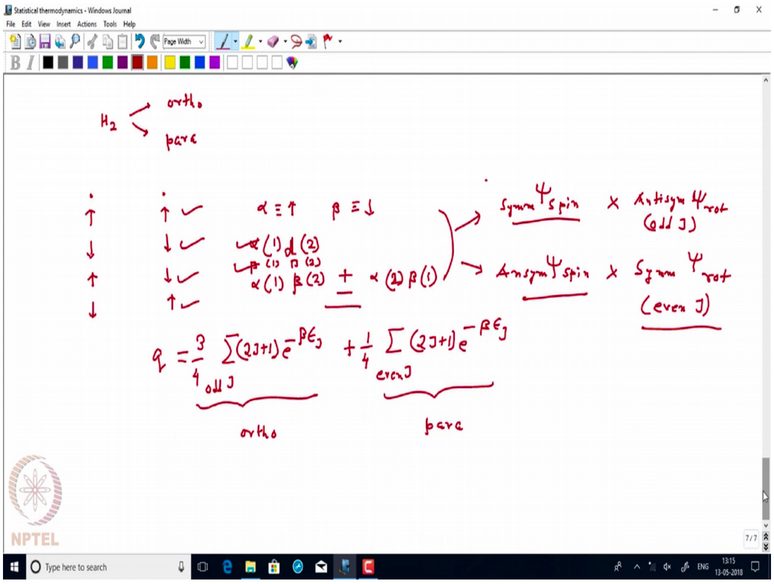

$$q = \underbrace{\frac{3}{4}\sum_{\text{odd } J}(2J+1)e^{-\beta\epsilon_J}}_{\text{ortho}} + \underbrace{\frac{1}{4}\sum_{\text{even } J}(2J+1)e^{-\beta\epsilon_J}}_{\text{para}}$$

One is called the ortho hydrogen and other one is called the para hydrogen. Now, what is or what are ortho and para hydrogens? Now, you can think that fine I have two hydrogen nuclei and of course, two electrons and these nuclei can actually have. So, it is basically proton and protons at fermium. So, I have actually two spin half particles.

Now, depending on their arrangement I can have both spins up, both spins down, one spin up, one spin down and it can be on two ways the spin can be down and this spin can be up. Now, again protons are doing fermions. These are basically indistinguishable particles and then, according to policy expression principle, you can actually have total there are four combinations. So, you will get basically total four states and what are the four states? So, you will get you can see that after interchange of any two nuclei if the total wave function is I mean not the total wave function, first let us focus on the spin part.

So, if we let us say if I just call this as alpha spin as the up spin and beta spin as the down spin, then you can easily figure out that if I have nuclei 1 in alpha state and nuclei 2 in beta state, if I just change these two numbers 1 and 2, it does not change the total spin part of the wave function, but if I have something like alpha and beta. So, this kind of combination, then I have a problem because nuclei distinct is indistinguishable. So, you cannot say which one is up spin and which one in down spin. So, in order for that what we do is that we take the symmetric combination as well as the anti symmetric combination. So, alpha 2 beta 1 and also, the minus combination and similarly here for this thing will have beta 1 beta 2.

Now, this combination as well as the symmetric combination, these three actually forms a symmetric spin wave function spin part of the wave function and then, the minus combination gives you the anti-symmetric spin combination. Now, since protons are also fermium, so the total wave function will be has to be basically anti-symmetric. So, the symmetric spin part goes to the anti-symmetric space part and in this case actually it will be anti-symmetric rotational part.

So, basically we are talking about the symmetric part of the speed and anti-symmetric part of the spin and as anti-symmetric part if we have the anti-symmetric part of the spin, it will go with the symmetric part of the psi rotation. So, you can actually use it slightly different rotations and we could write it as symmetric psi spin psi anti-symmetric psi spin something like that. Now, this anti-symmetric psi spin is actually related to the odd J values and the symmetric is related to the even J values.

Now, you will see that for every like if I write the total wave function or in this case, let us suppose that if I write we are talking in terms of the partition functions, the partition function which is the sum over 2J plus 1 into e to the power of minus beta epsilon J and sum is taken over all J. Now, I can actually divide this sum in two parts. One is basically I can sum over odd Js plus I can also sum over even Js into 2 J plus 1 e to the power minus beta epsilon J. And then, you see that all this even Js which are basically associated with the symmetric psi rotation, but the anti-symmetric spin part, the statistical weightage for that will be one-fourth only and for this actually will have 3-4 statistical origin because you have the symmetric spin part, you get 3 types of combination because it is alpha alpha beta beta and a symmetric combination of alpha beta like alpha beta plus beta alpha. Thus, we see that these wave functions are these partition function corresponds to the, it is ortho hydrogen which are basically sum over the odd rotational function and these corresponds to even functions which are basically known as para hydrogen.

So, that is why at room temperature statistically if you measure, you will get always three-fourth of ortho hydrogen isotopes and one-fourth of the para hydrogen isotopes and this is the origin of this rotational number. So, that is how it basically comes and you have to be very careful when you calculate this rotational partition function and that is how the symmetry number appears. So, the origin of symmetry number is a very much quantum mechanical in nature.

It comes from Pauli Exclusion Principle for fermions. Now, for our most of the discussion we will not use this symmetric number too much until and unless we encounter a problem where actually we have something like a homo nuclear diatomic system for which this symmetry number is required. Now, let us talk about the Vibrational Partition Function.

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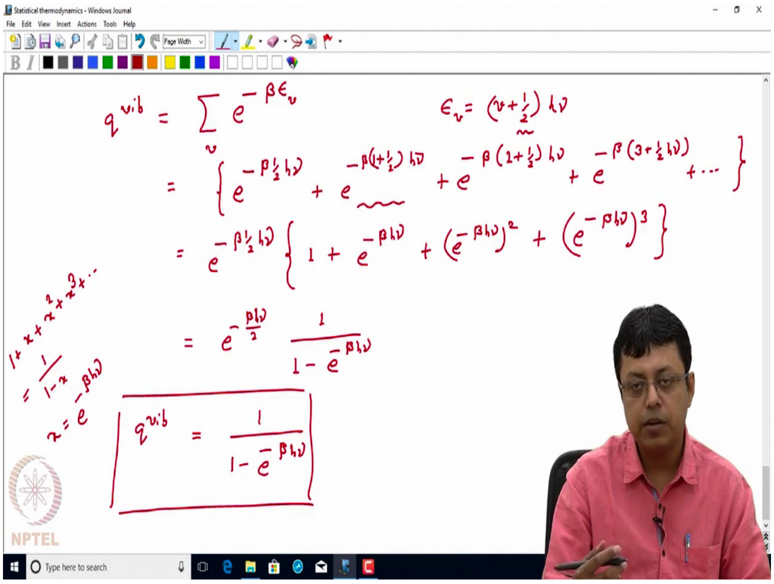

$$q^{vib} = \sum_{v} e^{-\beta\epsilon_v} \qquad \epsilon_v = (v+\tfrac{1}{2})h\nu$$

$$= \left\{ e^{-\beta\frac{1}{2}h\nu} + e^{-\beta(1+\frac{1}{2})h\nu} + e^{-\beta(2+\frac{1}{2})h\nu} + e^{-\beta(3+\frac{1}{2}h\nu)} + \dots \right\}$$

$$= e^{-\beta\frac{1}{2}h\nu}\left\{ 1 + e^{-\beta h\nu} + (e^{-\beta h\nu})^2 + (e^{-\beta h\nu})^3 \right\}$$

$$1+x+x^2+x^3+\dots = \frac{1}{1-x} \qquad x = e^{-\beta h\nu}$$

$$= e^{-\frac{\beta h\nu}{2}} \frac{1}{1-e^{-\beta h\nu}}$$

$$\boxed{q^{vib} = \frac{1}{1-e^{-\beta h\nu}}}$$

Again q vibration is nothing, but sum over e to the power of minus beta epsilon vibration. Now, we know that epsilon vibration is nothing, but we have v plus of v is the quantum number and for vibration, we have zero point energy level and we can write it as h bar omega. You can write it as h nu whichever way you prefer and the sum is taken over v, but in this case actually I am not writing or replacing the sum by integration. The reason as we said that even at room temperature for a vibration something like few thousands of wave number, you see that predominantly the ground vibrational state is populated. So, it is basically a discrete energy level or few energy levels that are propagated and energy levels are not continuous compared to your k B T or 1 over beta.

So, we will just use the sum as it is now this half. So, what will be the partition functions like if I take v, so it is a sum. So, let us just calculate the sum like this. So, I am taking the sum over v. V is going from 0 2 0 1 to something like that. So, the first one will be e to the power minus beta half h nu, the second one will be e to the power minus now you can see it is 1 plus half. I am just writing it as 1 plus half in that way not 3 by 2 h nu. The third one will be e to the power minus beta. It will be 2 plus half h nu. So, that way we will have the sum 3 plus half h nu.

So, what we can do that half h nu term we can take common and then, inside bracket we will have 1 plus. Now, here for these terms, for the second term let us look at it. It will be e to the power minus beta h nu. Let me just write it like this. The third term it will be a minus beta 2 h nu. So, that term I am writing it as e to the power minus beta h nu squared and then, similarly the fourth term I am writing as e to the power minus beta h nu cube. We should use different brackets here and then, what we figure out here is that this is nothing, but the series 1 plus x plus x square plus x cube, this series and the value of the series is 1 over 1 minus x, where x in this case is e to the power minus beta h nu.

So, we can readily write it as beta h nu by two times 1 by 1 minus x and that is a to the power minus beta h nu. So, this is the vibrational partition function again. Sometimes the vibrational partition function is measured from the zero point vibration. So, you basically subtract that and then, calculate in that case you will see the expression for the vibrational partition function as 1 by e to the power of minus 1 minus e to the power minus beta h nu; so, when using this expression when we will be discussing the transition state theory.

Now, let us now look at, we have so far discussed: what are the values of the partition function or the molecular partition function. We talked about the translational part. So, which is this we talked about the rotational partition function which is this and then, we talked about the vibrational partition function and electronic partition function. Usually I mean will take to be 1 because the definition of partition function is for minus beta epsilon i, but we say that it is only the ground electronic state that is both weighted and that epsilon i what this is write it.

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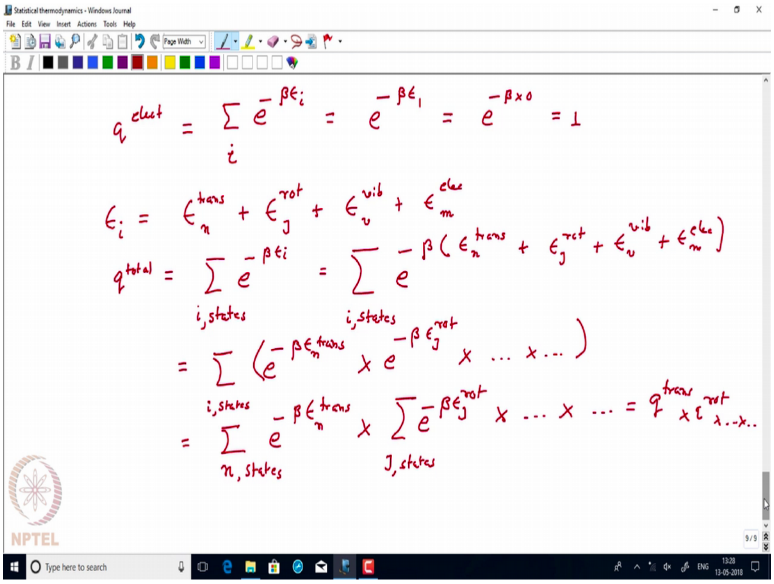

$$q^{elect} = \sum_{i} e^{-\beta\epsilon_i} = e^{-\beta\epsilon_1} = e^{-\beta\times 0} = 1$$

$$\epsilon_i = \epsilon_n^{trans} + \epsilon_J^{rot} + \epsilon_v^{vib} + \epsilon_m^{elec}$$

$$q^{total} = \sum_{i,states} e^{-\beta\epsilon_i} = \sum_{i,states} e^{-\beta(\epsilon_n^{trans} + \epsilon_J^{rot} + \epsilon_v^{vib} + \epsilon_m^{elec})}$$

$$= \sum_{i,states} \left(e^{-\beta\epsilon_n^{trans}} \times e^{-\beta\epsilon_J^{rot}} \times \ldots \times \ldots\right)$$

$$= \sum_{n,states} e^{-\beta\epsilon_n^{trans}} \times \sum_{J,states} e^{-\beta\epsilon_J^{rot}} \times \ldots \times \ldots = q^{trans} \times q^{rot} \times \ldots \times \ldots$$

So, what I am saying here q electronic that we say that it is only one state. So, it is sum over all the electronic energy levels e to the power minus beta epsilon i, but it is just only first energy level. So, beta epsilon 1, the ground state and this ground state energy if we take it to be 0 because it is just a choice of 0. So, then actually it becomes e to the power minus beta into 0. So, that becomes 1.

So, until analyze the electronic ground state is degenerated or something like say for radicals say I have an unpaired electron, then I will have a double state in the ground state in those cases, the partition function will be 2. So, because you can think that then I have basically a degeneracy of 2 and that degeneracy gets multiplied, but the other part is same. So, what we just learned is that what will be the total energy of the molecule. Now, as we talked about the translational case if we have some energy, let us say we gave you a particular example that if we have a total energy something like say 6 n square, this example 6 h square by 8 m l square.

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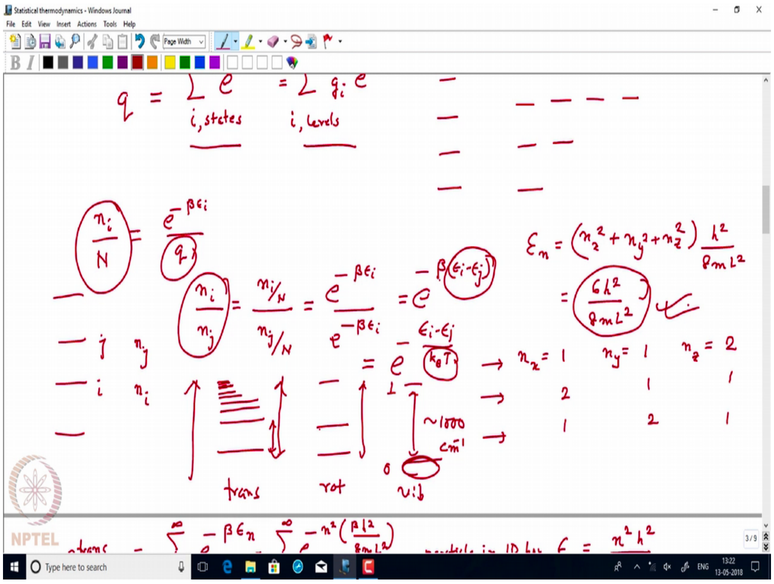

So, that is a energy level, but then we found that this is actually composed of 3 energy states and then, how we got it because actually we know that the translational partition function that in 3D is basically addition of the energies of 1D and that is why the energies are additive. That is why the partition function came as a multiplicative way and that is why we got basically e to the power 3 by 2 term which we derived at some stage, this 3 by 2 term.

Similarly, the total energy suppose if I am saying that I have some energy level of the molecule i, but that i corresponds to some translation of energy, some rotation, some specific translation energy, some specific rotation energy, some specific vibration and energy which means actually this e i corresponds to some translational energy, some specific and some rotational. Sorry we are writing the trans, wrote all these things as a superscript. So, let us follow this notation and the quantum number J and some vibrational partition function and some electronic partition function of course and let us denote for electronic quantum number, let us just say it is not i.

We have already used i here. Let us say we call it as some m. So, what we are saying here is that then in a similar token that we know that q total is basically sum over all these energy levels with all their degeneracies. If I am taking this sum over levels e to the power minus beta epsilon i, but then you can actually write epsilon i in terms of the translational rotational particle and vibrational, then you will easily figure out and you write that e to the power a plus b plus c is actually e to the power a times e to the power b times e to the power c that way.

So, then you can easily figure out that you have or we can actually use the state level here because we are just talking about the states right now and then, you can convert it into levels. So, I have sum over i which is taken over states and then, I am writing e to the power minus beta instead of epsilon i, I am writing epsilon n trans plus epsilon j rotation plus epsilon v vibration plus epsilon m electronic; so, all these energy levels.

Now, we can actually write this thing in the next step as sum over states e to the power minus beta epsilon n trans times e to the power minus beta epsilon j rotational times vibrational times electronic and then, we can actually write separate this term separately. So, we write them separately that you are taking sum over n first which is specifically the translational port. So, let us write it explicitly into then you will write rotational port which is e to the power minus beta e j rotation sum is taken over the rotational quantum numbers and again this is a state similarly for vibration, similarly for electronics.

So, you will get at the end of the day this is nothing, but q trans into q rot into q vibration into q electronic. So, all the partition functions will be multiplicative. Now, this is an important result which is a very straightforward result, but we will be using it quite frequently. Now, we have already discussed that, ok. So, what is partition function, but now this partition function is a molecular partition function and you can actually build up the macroscopic energies from that. Now, how do I approach that problem suppose I ask you this question.

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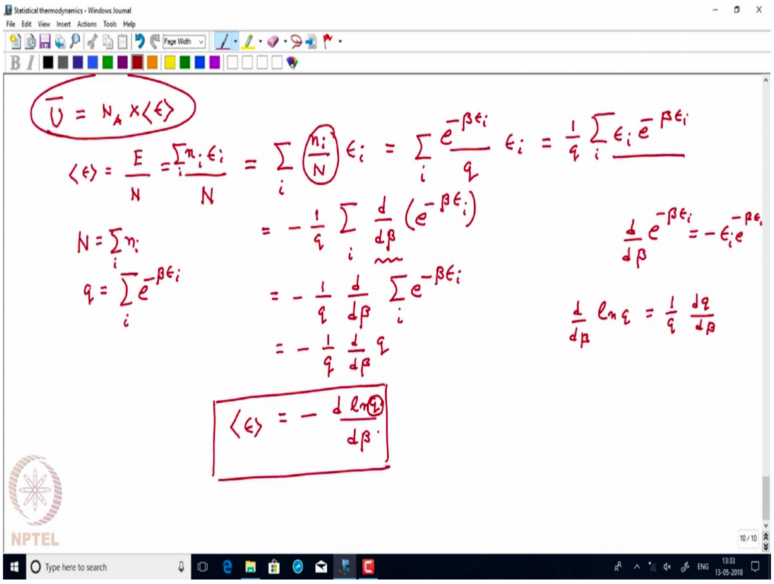

$$\boxed{\bar{U} = N_A \times \langle \epsilon \rangle}$$

$$\langle \epsilon \rangle = \frac{E}{N} = \frac{\sum_i n_i \epsilon_i}{N} = \sum_i \boxed{\frac{n_i}{N}} \epsilon_i = \sum_i \frac{e^{-\beta \epsilon_i}}{q} \epsilon_i = \frac{1}{q} \sum_i \underline{\epsilon_i e^{-\beta \epsilon_i}}$$

$$N = \sum_i n_i$$

$$q = \sum_i e^{-\beta \epsilon_i}$$

$$= -\frac{1}{q} \sum_i \frac{d}{d\beta} \left(e^{-\beta \epsilon_i} \right)$$

$$= -\frac{1}{q} \frac{d}{d\beta} \sum_i e^{-\beta \epsilon_i}$$

$$= -\frac{1}{q} \frac{d}{d\beta} q$$

$$\frac{d}{d\beta} e^{-\beta \epsilon_i} = -\epsilon_i e^{-\beta \epsilon_i}$$

$$\frac{d}{d\beta} \ln q = \frac{1}{q} \frac{dq}{d\beta}$$

$$\boxed{\langle \epsilon \rangle = -\frac{d \ln \boxed{q}}{d\beta}.}$$

What is the internal energy per mole? Can I write it in terms of the partition function? The answer is of course yes because the inner if we can actually calculate, what is the average energy per molecule has, then I can just simply multiply the average energy per molecule into the Avogadro number. So, this average has to be first calculated.

Now, let us see what this average is. Now, this average means again it is basically the total energy divided by the number of molecules and total energy already we know the total energies expression, it is nothing, but n i epsilon i and remember the number of molecules expression or sum over n i. Now, n i divided by the sum over n i is the probability which we talked about. So, this is nothing, but I have to take a summation here over i. Let us just skip this n as capital N only and then, what I am doing or watch carefully. So, I have a sum over i and then, I am writing this n inside this summation into epsilon i.

Of course, n is nothing, but sum over n i and then, what is this thing. This is the probability distribution nd that is nothing, but e to the power of minus beta epsilon i by sum over beta epsilon i which is q. So, q is nothing, but the sum over e to the power minus beta epsilon i and then, I have this sum over i epsilon i. So, I can take the q outside. So, it will be epsilon i e to the power minus beta epsilon i, but then you look at this equation if I take e to the power minus beta epsilon i and take the derivative with respect to say beta, then what I will get is, I will have minus epsilon i e to the power minus beta epsilon i.

So, we have here right now the epsilon i e to the power minus beta epsilon i. So, it will be a minus sign which is included. So, I can write it as minus 1 over q sum over derivative with respect to beta of this quantity e to the power of minus beta epsilon i. Now, this derivative is with respect to beta. So, this derivative as such does not depend on the summation differential operations are linear operations. So, I can actually take it outside the summation and I could just sum this quantity e to the power minus beta epsilon i and that is nothing, but q again. So, this is nothing, but minus 1 over q d d beta of q.

Now, what is this quantity 1 over q d d beta q. This is nothing, but if you take say l n q and then, take the derivative with respect to that. So, I have 1 over q and sorry if we have d d beta, sorry 1 over q. So, I will have d q d beta. So, this quantity is nothing, but d l n q d beta. So, thus we see the average energy per molecule is nothing, but this. So, now we can easily calculate the total energy or the energy per mole and that is a macroscopic quantity.

So, if you know the molecular partition function beta, of course you know this is a temperature derivative is 1 over k B T. So, if I know this molecular partition function, I can actually calculate the macroscopic properties. aAnd similarly, we can actually calculate many other properties like say entropy or the molar entropy, we can calculate the internal energy you have showed and then, you can calculate the Gibbs free energy and once we calculate the Gibbs free energy from that actually we can also calculate the equilibrium constant.

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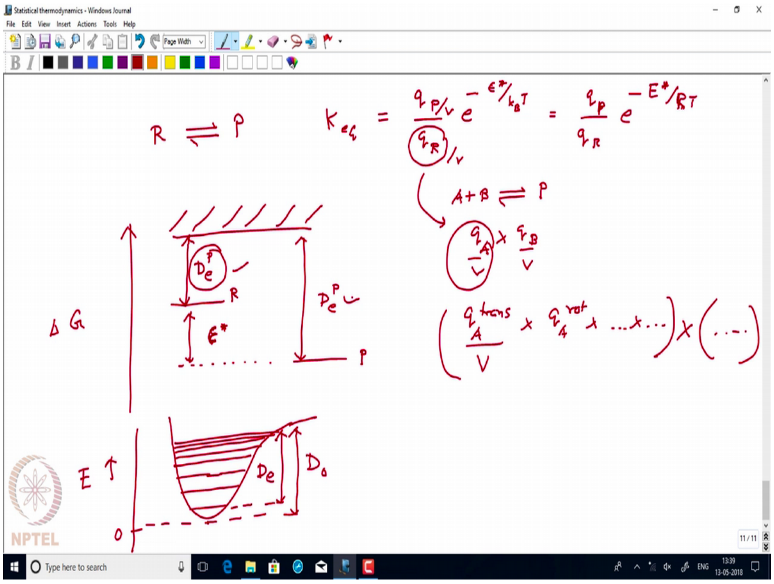

$$R \rightleftharpoons P \qquad K_{eq} = \frac{q_P/V}{q_R/V}\, e^{-\epsilon^*/k_BT} = \frac{q_P}{q_R}\, e^{-E^*/RT}$$

$$A+B \rightleftharpoons P$$

$$\frac{q_A}{V} \times \frac{q_B}{V}$$

$$\left(\frac{q_A^{trans}}{V} \times q_A^{rot} \times \ldots \times \ldots\right) \times (\ldots)$$

Now, suppose I have an equilibrium which is between some reactants is going into products and then, for that equilibrium and just writing the equilibrium constants, this now suppose there are sum in a free energy diagram. I have suppose the reactants energy levels are here, the product energy levels are here. So, what you can show I am not showing it. I am doing the derivation right now. So, you can actually have a look at any standard physical chemistry textbooks which are referred to you.

So, in some sense you can think of the process going from say reactants to products as this. So, you are going, you have a dissociation energy which dissociates the reactants. Suppose this is a continuum of energy and similarly, you could also think about the dissociation energy for the products and can show that this and this is basically Gibbs free energy change and you can show going from reactant to product. If I write the equilibrium constant in terms of the reaction questions which are related to Gibbs free energy change, then you can show that finally if this energy difference of Gibbs free energy difference if we write it as a say epsilon star or something like that, then we can write the equilibrium constants in terms of the partition functions of the product divided by the reactant times e to the power minus epsilon star.

We are writing this notation epsilon star by k B T if we write a more notation. So, you should use instead of k B T, you should write r t, but similarly you write as capital E for the molar notation, but whatever it is the there is a point to discuss here. First of all, you can have many reactants, but if I have suppose A and B at the reactants it is suppose it is by molecular reaction giving you a product and which is in equilibrium with A and B. So, then this reactant partition function is nothing, but a partition function of A times partition function of B and that is obvious.

Secondly, this is although unwritten it as a partition function. Strictly speaking this is partition functions per unit volume. So, the reason is remember that what will be the partition function of A. It has translation rotation and vibration, but translation always comes with partition function part. You need volume because if you remember that the translational partition functions, let us go back here.

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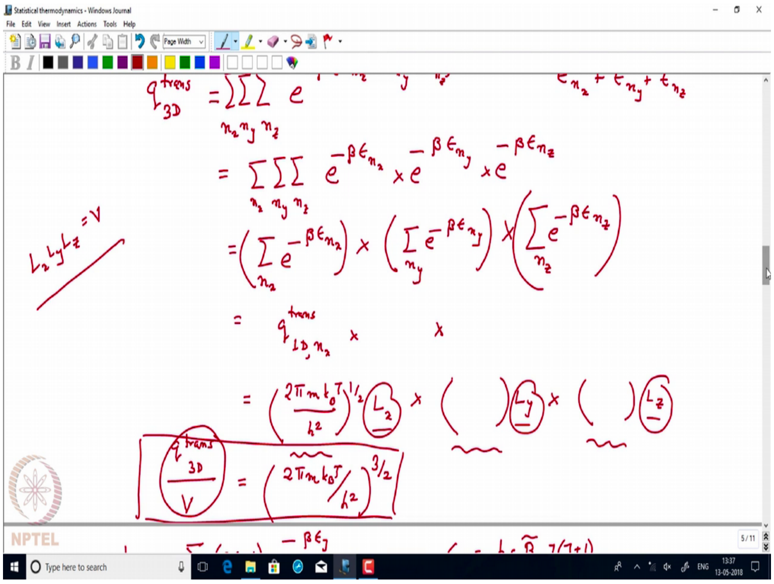

$$q^{trans}_{3D} = \sum_{n_x}\sum_{n_y}\sum_{n_z} e \qquad \epsilon_{n_x}+\epsilon_{n_y}+\epsilon_{n_z}$$

$$= \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\beta\epsilon_{n_x}} \times e^{-\beta\epsilon_{n_y}} \times e^{-\beta\epsilon_{n_z}}$$

$$= \left(\sum_{n_x} e^{-\beta\epsilon_{n_x}}\right) \times \left(\sum_{n_y} e^{-\beta\epsilon_{n_y}}\right) \times \left(\sum_{n_z} e^{-\beta\epsilon_{n_z}}\right)$$

$$= q^{trans}_{1D,n_x} \times \qquad \times$$

$$= \left(\frac{2\pi m k_B T}{h^2}\right)^{1/2} L_x \times \left(\quad \right) L_y \times \left(\quad \right) L_z$$

$$L_x L_y L_z = V$$

$$\boxed{\frac{q^{trans}_{3D}}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}}$$

So, we had this L x L y L z which actually together gives you the volume of your macroscopic system and that volume will always divide by their translational partition function. So, the volume part always gets associated with translational partition function. It makes sense because the energy levels depend on the volume of the container because in particle in a box model, it depends on the length of the containery 1D system. So, similarly in 3D system, it depends on the volume of the container, but rotation and vibration and electronic degrees of freedom these are internal motion and they do not depend on the volume.

So, when you write this q a as say q a translation q a rotation in that way and q a vibration and q a electronic, you divide, you associate this volume with the translation volume and then, you calculate it. Similarly, for q b also you have to do the similar thing. So, that is how we calculate the equilibrium constant. One more point here to note that this dissociation energy means this is this experimental dissociation energies. There are two kind of dissociation energies.

Suppose I have bond of vibration and the bond is dissociating, so usually the energy levels, the potential for one vibration is harmonic relation. So, there actually you have the zero point energy as we just discussed just like harmonic oscillators. You have a zero point energy and then, suppose you are measuring if we measure the energy from the zero potential, that energy you call it as d0 as opposed to the energy you have just drawn which is the experimentally determined quantity which you know call as d e.

So, these d e actually already includes that zero point effect because you are not starting from your 0 of energy, but you are if I call this level as your 0 of energy of the total energy, so this is supposed to electronic 0 of energy and then, you have the vibrational manifold on top of it on which vibrational manifold will also have each vibrational level, also have a rotational manifold and each rotational manifold will have translational manifold. That is how you describe the total energy of the system and then, you see here that you have d e here. So, these are all actually d e.

So, it is basically the difference of the zero point energies of the reactant and the product that is very important thing. So, it is not that between the 0 0 difference, it is basically taking into account the zero point energies always. Now, we will stop our discussion on this part where we discussed briefly the statistical mechanics of statistical thermodynamics. Again from a very basic point of view, we only talked about the molecular partition function. So, what we learned in this lecture is that what we need to remember which will be necessary that we got a formula for 3D translational d your freedom just writing 3D version.

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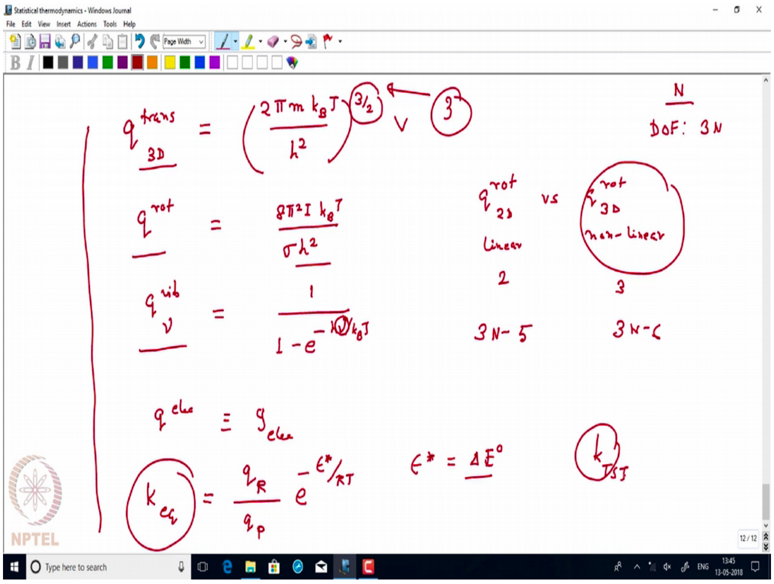

$$q^{trans}_{3D} = \left(\frac{2\pi m k_B T}{h^2}\right)^{\boxed{3/2}} V \leftarrow \boxed{3}$$

$$\underline{N}$$

DoF: $3N$

$$q^{rot} = \frac{8\pi^2 I k_B T}{\sigma h^2}$$

q^{rot}_{2D} vs $\boxed{q^{rot}_{3D}}$

Linear | non-linear

2 | 3

$$q^{vib}_{\nu} = \frac{1}{1 - e^{-h\nu/k_B T}}$$

$3N-5$ | $3N-6$

$$q^{elec} = g_{elec}$$

$$\boxed{k_{eq}} = \frac{q_R}{q_P} e^{-\epsilon^*/RT}$$

$$\epsilon^* = \underline{\Delta E^0}$$

$$\boxed{k_{TST}}$$

So, it is nothing, but 2 pi m k B T divided by h square raise to the power 3 by 2 into volume and then, we have the rotational partition function which is 8 i square i k B T divided by h square and then, we have also the vibrational partition function and that is 1 over 1 minus e to the power minus h nu by k B T and remember that there could be many vibrations in the molecule like that would be. So, then you have to calculate the partition function for each degrees of freedom because usually you have 3 rotations and you have for a linear molecule will have 2 rotational degrees of freedom for a non-linear molecule in our 3 rotational degrees of freedom.

So, we will ask you to figure it out in a problem set. So, what is this we have calculated and how we can distinguish, what will be the different rotational partition function, if there is any difference between 2D and versus rotational partition function for 3D meaning, if it is a linear molecule and if it is a non-linear molecule, how the rotational partition function will change and also remember that we introduced our symmetry number and we said that for a diatomic molecule or for a symmetric molecule linear symmetric molecule, we will have to introduce this signal.

Now, one thing to you can easily figure out that this few rotation must be for it is a derived for actually linear molecule. The reason is you can see here just look at the factor here. So, it is basically 3 by 2 here. So, I have in the denominator h bar squared if it is 2D problem. So, then it will be basically 2 by 2. So, I will have h bar squared. So, it readily tells you that it is not 3D version. So, you will be asked to calculate the 3D rotational partition function and then, you have vibration by vibration.

Again you have suppose if my molecule of the system has it same particle system, each molecule has suppose n atoms or something like that, so the degrees of freedom will be 3 n. So, then it will be free translation depending on the molecule whether it is linear and non-linear. By the way these three is giving rise to this 3 by 2 factor. So, I can have 2 degrees of freedom or 3 degrees of freedom. So, you will have 3 n minus 5 or three n minus 6 vibrational degrees of freedom. So, each vibration will have a characteristic vibrational frequency nu. So, what I am writing it is actually for a particular vibrational degrees of freedom.

So, if you have suppose for example two vibrations, then this total vibrational partition function of vibrational partition function for one vibration times, the vibrational partition function for the second condition and a good thing with partition functions is that these are all multiplicative because the energy is additive and electronic partition function. We usually said this is equivalent to basically you can write it as the electronic degeneracy because the other part is just 1.

So, it will be identical to the electronic degeneracy which is most of the cases will be 1 and finally, we also talked a little bit about an expression for equilibrium constant where we wrote it as the equilibrium constant is nothing, but can be expressed at the partition function of the reactants. And, the partition function divided by the partition function of the products times exponential minus e star by keyword e star is the difference. Some textbook actually write it as delta e 0. So, the delta denotes is a difference in energies and 0 says that it is basically difference in zero point energies.

So, we will conclude our discussion here and we will be using all this expression heavily in when will be calculating the rate constant for the from the transition state theory, where it will have this concept of an equilibrium between reactants and our transition state that we will hypothesize that it exists briefly before other reactants are going into products and will cleverly introduce the same concept there. Then, we will calculate the partition functions and we will see how one can calculate a rate constant from the thermodynamic parameters which are our time independent parameters which is a very interesting theory. It is called Transition Set Theory. We will be talking about it in details later, alright.

Thank you.