Advanced Chemical Thermodynamics & Kinetics
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Lecture-30
Unimolecular reaction 02

Alright so today we will discuss the more detail the mechanisms for Unimolecular reaction. So, as we know that for bimolecular reaction or like elementary reactions can be actually either bimolecular elementary reaction can be either bimolecular or it can be unimolecular.

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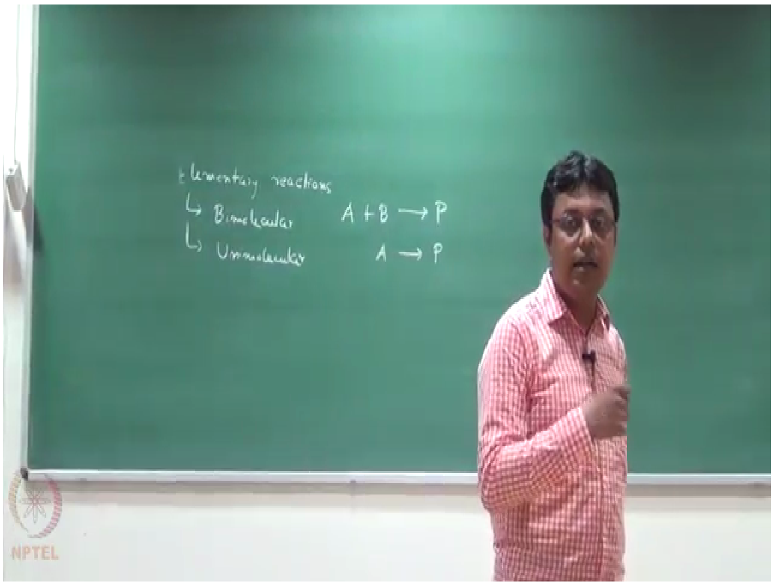

So, in bimolecular reaction what happens is that, there are two reactants that gives you the product and in a unimolecular case s will react and gives product.

So, the probability of three body collision is less and that is why we say that there is no such trimolecular reaction, but there are certain examples the very few examples where actually you can have ibody collisions. But we will restrict our discussion on bimolecular and unimolecular reaction when the reaction is happening three obvious that there are basically collisions between reactants that will give the products. Now we can do it in two ways one is that we can actually solve the equations of motion and do the dynamics, but that is a more rigorous right because if you think that we have to basically solve the either the classical Newtonian equations of motion or eco mechanically the Schrodinger equation of motion Schrodinger's equation.

So, then the problem will be in a macroscopic system you have huge number of atoms or molecules so which we cannot solve. So, an alternative book is basically looking at the problem from my statistical point of view and that was the essence of transition state theory which we discussed already, but we will discuss in a more rigorous way now this requires some knowledge of classical statistical mechanics. So, which we will skip, but we will give an handout which you can follow and see how basically you can actually connect it to the classical partition functions.

Now, before we go to the unimolecular reaction we will first discuss the bimolecular reaction as I said. So, for a bimolecular reaction if you remember that there are two molecules which are basically colliding with each other and then the question was that what?

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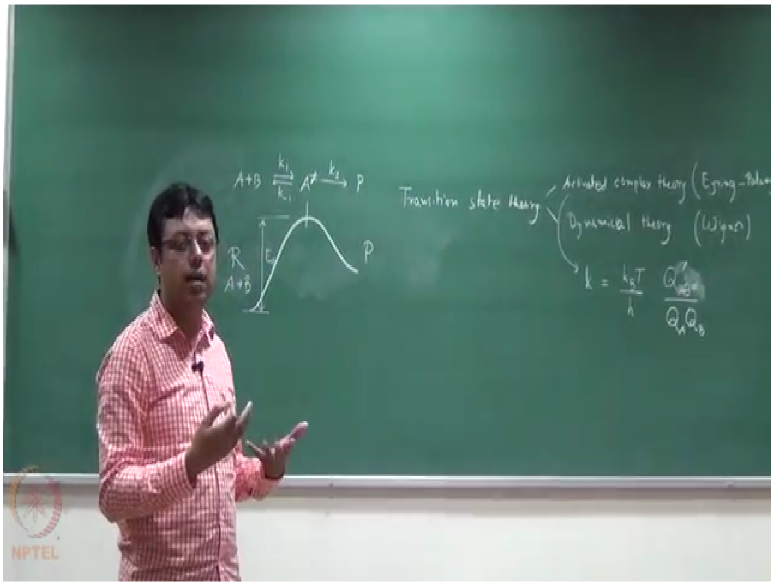

Student: (Refer Time: 03:01).

Eyring and Polanyi visualized is that there is a potentially energy surface this is basically potential between the molecules, which is the reactant species and then basically this side is the reactant side and this side is the product side. So, reactant means here I have A plus B and the idea is that, if these overall energy which energy which is basically you can see energy which is along the line of centre of the two species. If that actually exists around certain amount let us let me call it as say E 0 which is the threshold energy then I will get a product.

And then they said that everything happens basically the dynamics we can actually think of going to something like a transition state who which actually exist in between the reactants and the products. In the on the potential energy surface which means actually this reaction A plus B going to product can be thought off as going to a transition state. And then if you remember that the Eyring and Polanyi, they say that we can actually think of equilibrium it is more try to call it as a quasi-equilibrium between the activated complex and the reactants and then the activated complex is basically forming the product with some rate constant.

And the challenge was basically to model this system and then they said that fine since there is a equilibrium they say that always you can write an equilibrium constant in terms of the partition functions. And then they use the statistical mechanics, but the entire point here is that when they formalized this theory which is known as transition state theory.

In the sense that there is a transition state which we are denoting by this notation dagger that exists between the reactants and the products, but the version which Eyring and Polanyi gave is more correctly known as activated complex theory. In the sense that they kind of visualized that there is a activated complex that exists in between which I am denoting as a dagger, and if I know the statistical mechanical properties of this activated complex I can calculate the rates.

So, it is more widely known as activated complex theory which we discussed or which is also discussed in any elementary test or physical test, but later people realized that this version which was given by Henry Eyring and once as well as Karl Polanyi. So, I am just writing it Eyring and Polanyi later on people kind of realized that though this activated complex is actually situated on a particular point of potential energy surface. In the sense that it is coordinate is fixed and the way we derived it that the things are moving from left to right which means actually it is momentum is also fixed because I have a fixed energy.

So, if you have a fixed position and fixed momentum which means actually it is inherently a classical mechanical theory ok. Any transition state theory is actually classical mechanical theory, but when Eyring and Polanyi was computing the rate constant using the partition functions they actually used the quantum mechanical partition functions.

Using Schrodinger equation and basically for transition and partition function they used a (Refer Time: 06:53) and so on. Now the question was this was actually this is a very like very certain point and then the physicist Wigner who is very well known for his work on neutrinos and many other in your chemical physics. He say he pointed out around the same time that it should be a classical theory, but that time it was not very popular people realized it much later that what is what was Wigner point and that that is what we are going to discuss.

Wigner said actually this is a dynamical theory in the sense that although we are doing statistical mechanics like dynamics is kind of inherent theory. And I can actually solve classical equation of motion you show that ultimately it will reduce to the same activated complex theory.

Now just to begin with this activated complex theory already they showed basically we consider an equilibrium and there will be a delta G for the equilibrium because in equilibrium constant you can write it as e to the power minus delta G by kBT. And that delta G you now connect it to partition functions and from there if you just do an analysis and also this k 2 k 2 is basically was the activated complex is formed it is basically the rate at which the activated complex is giving you product.

And Eyring and Polanyi thought that it will be a like this molecule will have 3 N minus 6 or 3 N minus 5 degrees of freedom one vibrational degrees of freedom which is very weak and which is along the reaction coordinate that will give you the product and then they basically came up with a relation, which is the very celebrated equation.

So, they said that the rate constant for the bimolecular reaction we can show that this is basically a combination of constants k B is the molecular constant T is the temperature absolute temperature h is the Planck’s constant. And then it is nothing, but the partition function for the transition state you can actually write it as Q A B dagger divided by the partition function of the reactants.

But this Q A B dagger is like different and we use the prime notation in the sense that it is not a all the partition function one degree of freedom is actually taken out. And that is what they shown and that is what agreed in textbook also shows now there are actually they said that there is no such dynamics it is just thermodynamics in the sense that there is an equilibrium ok.

And all the equilibrium I am pasting to actually partition function. Now let us say what Wigner said or how the Wigner basically visualize the problem now this is the bimolecular reaction although I have shown it as a one dimensional potential energy curve in reality it will be a multidimensional potential energy surface and what Wigner said is that fine.

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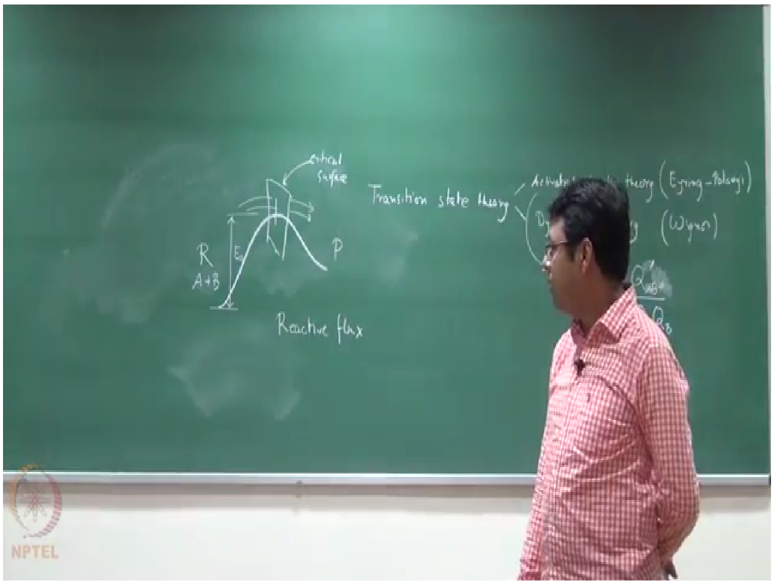

Let us visualize that I am having a two regions similarly, I have reactant region and I have product region I can use the same figure. And then there is some kind of surface which is lying at this region which is closed to the transition state region this he called as something like a critical surface. So, the critical surface basically tells you that if trajectories come from left. And if there is no re crossing re crossing in the sense you can think that there is a surface and there can be reactive current curves, which actually come back they actually comes to the product area tensile.

But if I assume that there is no re crossing then all this trajectories which are passing through this surface will give me product. Now in the dynamical theories of using polar dynamics using something known as reactive flux we actually compute these trajectories by solving Schrodinger equation of motion.

But that is a very tedious job because we cannot solve it for like for we will have to basically do a sampling or for many initial condition of a reactants and that is a tedious job. Now what Wigner said himself fine let us see that fine I have a transitional state here and all I need to know ok. Is how many trajectories are basically, what is the fraction of molecules which are crossing this surface ok. Now he had in his mind or back of his mind very much dynamical picture in the sense that there are trajectories, but how can I can actually avoid computing the trajectories that is the internal picture.

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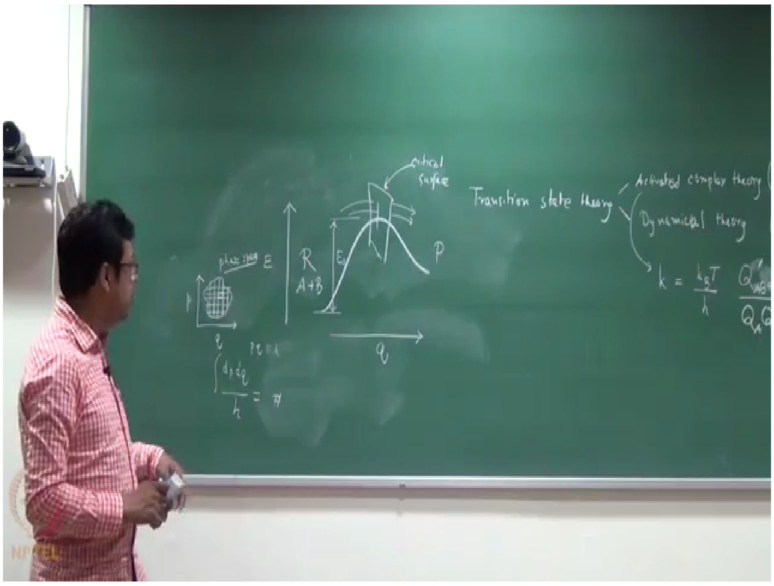

Now, let us try to understand now here the picture what I have drawn is basically this axis is a poor image right it is basically the position of coordinate and this axis is the energy. But you can actually cast everything you phase space in a sense that I can actually think that for example, for a one dimensional system right. I can actually have different position I can write the position as q at different times this will actually describe the dynamics of the system. Alternatively I could use the position and the velocity which is basically the lagrangian formalism or I could use the position and momentum which is the Hamiltonians formalism.

And so basically what I am trying to say here is that I can actually instead of writing it as I have q verses t curve I could have actually cast the problem as a p q t p q notation in the sense that I can cast the entire thing in phase space ok. Now Wigner said that let us change the there is a phase space and there is a phase space volume and I have a surface all I need to calculate what is the fraction of the molecules which are lying here so that I can calculate by calculating a phase space volume how?

Now, basically here we are calculating the number of states right or basically the number of molecules we can show suppose I have a phase space area something like that what I am saying here is that this area is allowed for that critical surface. Now how will you calculate the number of states which are lying here the fundamental assumption here is that in the minimum area in the phase space, this combination p times q which has a dimension of action ok. Will be something like equivalent to the Planck's constant now here we are kind of using the notion of quantum mechanics that in a add on way this is the only quantum part here ok.

In the sense by you will now say that fine I will just divide this phase space area each of them has basically area h and then what will be the total area total area will be find. So, I have say dp dq will be the differential area I will integrate over this thing and if I divide my unit area, then I should get the number how many number of squares are lying here as simple as that ok.

Now this is not actually this is not a one dimensional problem for a one dimension it will have basically p q 1 phase space right, but then as we can see that if I actually extend it for a system which has n atoms then I have 3 N positions and 3 p, I mean 3 N momentums also right. So, basically it will be a 6 n dimension problem clear so we will not try to draw it, but the idea is the pretty same that fine I have some differential area here.

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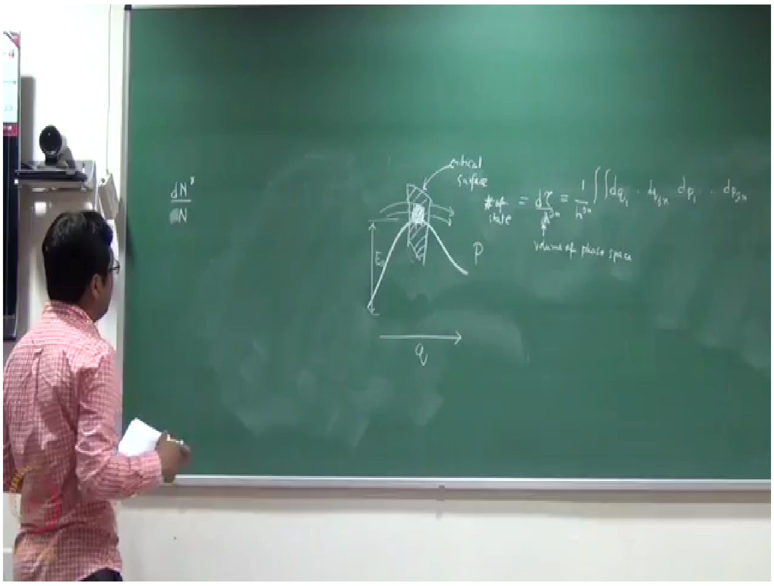

First I will calculate that area and then I will calculate the entire area in the sense that I will calculate the area and divided by the correct dimensionality you calculate the number of states which basically tells you the number of states which again is basically the fraction of molecules which are there alright.

So, let us try to calculate it so what we are saying is that I have a surface I have to calculate the entire surface which is the critical surface ok, but let us first consider a small sub surface there I am asking the question what all number of states ok. So, this number of states I can easily calculate so this is basically I have for any (Refer Time: 16:10) volume I am just writing it in more mathematical way. So, this is suppose volume of phase space now how you calculate the volume I said that my 3 are 3 N coordinates and then there are 3 N conjugate momentums.

So, coordinates I am writing as d q 1 to d q 3 N and then the p 3 N conjugate momentum then I have to integrate and there are 3 basically 6 way of integrations. So, that will give me the total volume and with this total volume now if I divide by the volume of each unit cell then I should get basically the number of states for the given volume.

Now, for one dimensional if you remember each E q combination was giving me a dimension which is h which is an area right here each d q combination will give me h. So, 3 N p q combinations will give me actually h to the power states ok, so if I divide this thing by h to the power 3 N that will give me the total number of states.

Now, what I am going to do is that I will first try to calculate what is the fraction of molecules, which are basically here and then I will integrate over all the critical surface ok. And I am assume that this fraction will be of course, connected to the reaction now let us first try to calculate this fraction see this differential fractions. So, what I am trying to say here is that here I am using a notation which is star, now star means if I try to draw it again that I had a surface ok.

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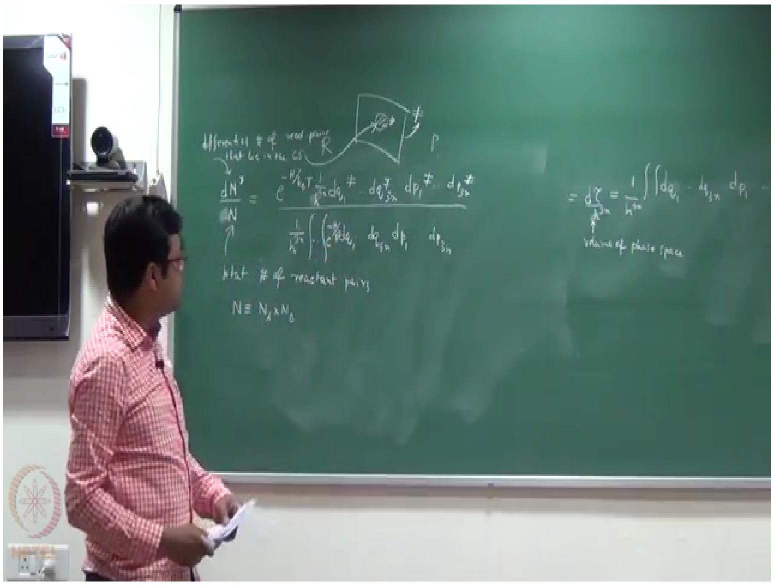

And in state of the surface I will just denote by dagger within the surface there is a sub-surface which right now I am just denoting as star ok. And then there is a global phase space area who where actually the reactants and products and everything is there ok. So, there is a reactant region there is a product region and then the surface is dividing and this surface is basically the transition state surface ok.

Now, let us first calculate what is this probability d n star right ok, so according to classical rule the number of states which the way we basically wrote it if you remember that if I write this fraction ok. So, by using statistical mechanics, it is the classical statistical mechanics ok, so that we can actually give you a hand out that basically says that I should take the Boltzmann factor and then.

So, what I keep here is this fraction this differential fraction what I am saying here will be depended on the Boltzmann fraction that actually comes from classical statistical mechanics, but you have also seen like in partition function I have always e to the power minus d 0 by d v t, but at this point this h is a classical Hamiltonian just classical.

And this of course, in order to calculate the number of states I definitely have h to the power 3 N something like that divided by n now what is n? N is basically the total number of states ok. So, n is nothing, but something like an integration which is exactly like that 1 over h to the power 3 N which has 6 n integration.

Now, look at the notation here, so what I did here is that I am using the dagger notation here just to clarify that this part is actually for n star which is basically lying here ok, but I am actually do not need n star I have to go to n star to dagger. So, which means I have to also integrate later on ok.

So, this is the small part of the critical surface at this one and then of course, this h to the power 3 N and h to the power 3 N will cancel ok. Now what is this N this N is nothing, but the total probability of states which are basically the starting point. Now the starting point if you remember that this N is nothing, but the total number of reactant pairs ok. And this d N start is basically the differential number of basically differential number of reactant pairs that are that lie in the critical surface basically this region clear.

Now, this is the meaning of (Refer Time: 22:53) now how you calculate the total number of reactant pairs. Now suppose if I have 10 molecules of a and 10 molecules of b if I calculate the pair it will be just 10 into 10 because each one will have a will have 10 b something like that ok. So, this N is nothing, but total number of A times total number of B as it was there clear alright.

Now, let us consider this part now this is nothing, but the and this e to the power minus H here now according to classical mechanics ok. So, this is nothing, but the partition function right partition function of what this is a partition function of everything. So, basically this is the partition function for the reactants q a or q b, but if you remember when we do this thing like we take a total partition function is basically the multiplication of translational rotational and vibrational and electron.

Now, translational we always do get a v because if you remember that is you there you get l for one dimensional and then you get a l cube or v for three dimensional. So, this cube which we will get is the translational partition function time's volume because the volume will sorry the total partition function times volume.

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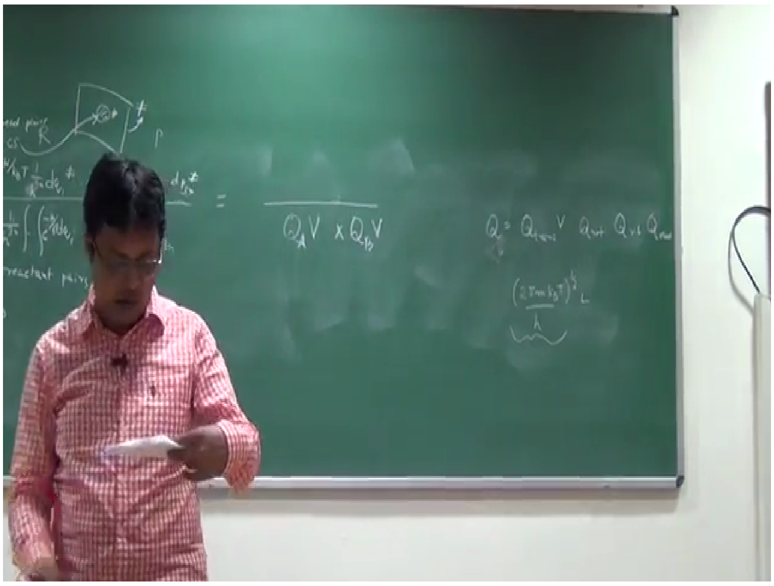

So, basically I can write it as this the denominator this is nothing, but partition function of a times the volume; volume of what volume of the content clear which one.

Student: (Refer Time: 24:50).

No so what I am saying here I have the total right. So, the total Q is Q translational ok. Now the expression for the Q is this if I divide it by v then I will get rid this ok, but the v will be always come because whenever you like if you start from a particle in a box. So, you get something like 2 pi m k T to the power half right and then there will be a L right.

If I extend it to 3 d so it will be 3 by 2 for a particle in cubic box then h cube and I have L cube so the v will always be there. So, this is this will write as Q trans and this is the v ok, so we should always say the transitional partition function per unit volume. So, here I am just including the formula and (Refer Time: 26:02) and this is nothing, but Q B into V right and the numerator is the same we are not changing anything.

Now, the question is fine what I have to do is that this point this is basically what I calculated is what is the fraction of molecules that are lying. In this small region of the critical surface and then I am asking the same question what is the rate at which they are crossing the surface ok, that will be basically the number of molecules which are there ok.

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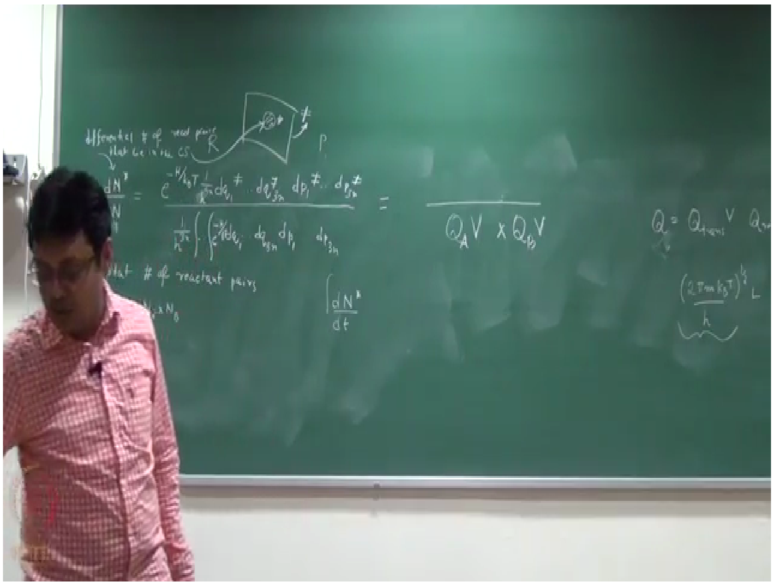

And the speed at which they are crossing meaning all I am now asking is that I know the rate will be somehow unit to this quantity d N star d t; how they are crossing where of course, d N star only they require some part of the thing. So, I have to eventual integrate it over the phase space for the critical surface not the entire thing ok, so we will do step by step.

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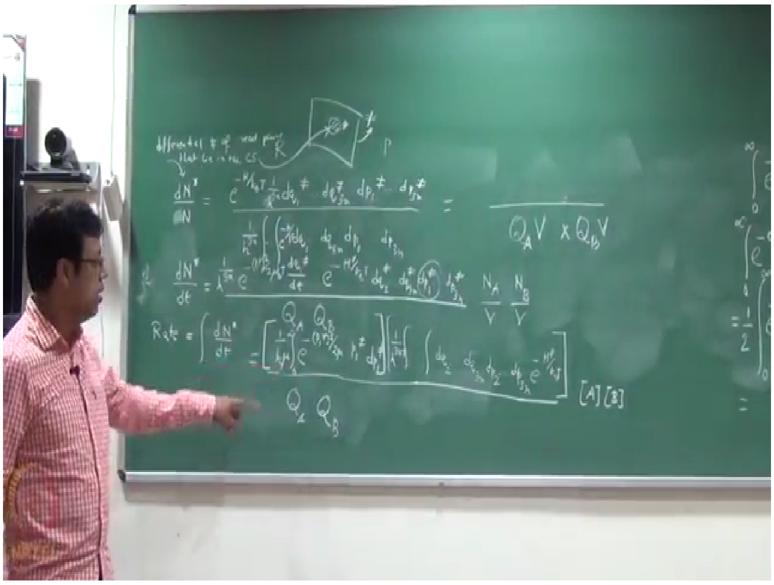

Now, first do this thing which is d N star d t now what is d N star dt now then we did not basically said that fine it is a very high dimensional thing right and it has basically many positions many momentum.

Now, only one degree of freedom is basically the reactive degree of freedom let us say this Q 1 dagger is the reactive degree of freedom. So, whenever I am taking a time derivative dt will be applicable only to this not any other like it is not a chain rule of differentiation, because all the character are changing positions and momentum are fixed ok.

So, I will take a time derivative for only this one clear ok; secondly let us try to understand what is this h as I said h is basically the total energy right, which is basically the kinetic energy plus potential energy and everything.

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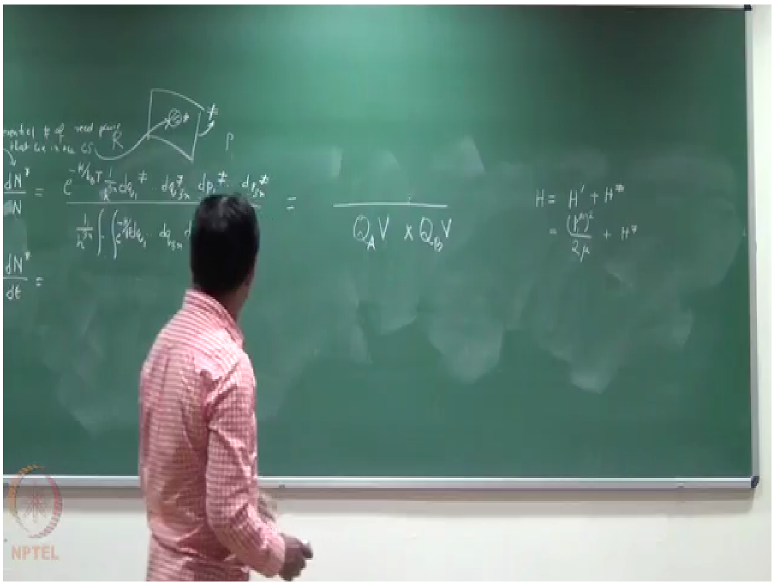

Now, this H I can write as some energy which is basically spend for that motion which motion which is basically the however, d q 1 coordinates is changing ok. Now, the picture is something like this that I have a surface right and I am considering a small surface right now and only one coordinate is changing which is Q 1 dagger why dagger because it is on the dagger space right now ok. Now anything related to a motion I can actually consider classical like kinetic energy; kinetic energy expression is e square by twice n right, but this is associated with only the P 1 (Refer Time: 29:29).

So, it is basically P 1 dagger that square by twice n, but this is not n I am just using some reduced 1 plus the rest of the thing the rest of the thing basically describes Q 2 to Q 3 N and all this things associated ok. So, the energy I am just partitioned I am saying that, due this crossing, which is basically the reactive crossing I have some energy and that is written clear ok.

Now, let us come back here ok, so what I have I have e to the power minus h by k b t, but that h I have already told that it is partitioned how that it is basically h prime plus h dagger right ok. And I am just following from here to here I have 1 N in the denominator that N I can bring it here I eventually what I do is that I just have n is nothing, but N A and N B ok.

So, this N I am here also what one over N right I am taking the time derivative from the entire thing ok, so the next step what I am doing is that d dt of this entire thing ok. So, that will give me 1 N that I am just taking there and already I said that it is reactant pairs N A times N B and I had actually 2 vs the denominator I can write divide it by V this I am divide it by V. So, in the denominator I have only Q N thing which are partition functions parameter clear.

Now, let us look at the numerator I have 1 h to the power 3 N e to the power minus h by kBT and then there will be a time derivative which is acting only here ok. So, what I am doing is very cleverly is something like this is I have e to the power minus h prime that is nothing, but P 1 dagger square by twice mu right ok.

And then I have this dagger we have to first let me first the constant h to the power 3 N ok, then I have this kind, but that I am write it as dq 1 dagger dt because that is the only thing that is changing rest is the same now what was my rest the rest was e to the power minus I already have taken care of h prime. So, so I am left with h dagger by kBT right and what are left I have dq to to dq 3 N right and I have dp 1 to dp 3 N these are all dagger clear because dq 1 already I have taken here clear ok.

Now the next thing is as I said that this is basically rate, which describe the rate due to this region, but I have to basically integrate over the entire ok. I basically I have to integrate then this thing which will be the rate by definition because the rate by definition is what are the number of what are the probabilities or the fraction of the molecules ok. That are lying here, but remember that fraction of the molecules lying in the critical surface automatically means that this is basically the probability of the molecules those have the energy which is crossing the (Refer Time: 33:47) ok.

Second thing is then I am calculating rate so it is not the number, but at what per unit time how they are change that is why I have to take time derivative. So, the rate of the reaction should be nothing, but this quantity which I how to get ok, but then I have to integrate it over the all the phase base, because I have to now said this is the coordination and then I am calculate it ok. Now here is the thing let me it integrate it, but before integrating if you see here what I am doing. So, look at what is NA by V this is basically density of a similarly NB NY B is density of B right so what I will have is 1 over QA QB actually will be there.

And eventually I have A into B just by molecular function now what is the numeric now do that it very careful I will integrate it this equation ok. But I am iterating fit level in the sense and h to the power 3 N that I will split as h and 3 N minus 1 ok. So, let me just write this thing h and then I am mescal integration for the P 1 Q 1 coordinate and one just a problem I cannot actually bring this P 1 here. And I will just integrate that is the thing, but look at it I have dq 1 dagger dt what is P 1 P 1 is momentum right or P 1 dagger means actually mass times velocity now velocity is 1 dq dt these are all dagger ok. So, this dq dagger dt is nothing, but P 1 dagger divided by mu ok.

So, I will just write it that I have e to the power minus P 1 dagger square by twice mu just following carefully add one extra mu reduce must that I am just putting outside the integral is just a constant. Then I am left with P 1 dagger because it was P 1 dagger by mu and then there is a dp 1 dagger clear this is just one integration, but there will be 3 N integrations actually there are 6 n integration basically ok. So, all others I will just write it together meaning I will have 1 by h to the power 3 N minus 1 all these things which is starting from dq 2 to dq n dq 2 to dp n with e to the power minus h dagger by kBt.

So, basically I partition the energy one energy was associated with the kinetic energy and the other energies are I do not care which are associated with the positions and the conjugate momentums excluding the particular coordinate. Now this itself as you can see is basically another partition function which has one degree less because that degree I am calculated separately and how and this is the separation this is the separation clear and here I have A into B clear right.

Now just I have to solve this integral now again so what is the range of the integration? So, I am having momentum here the momentum should have all possible ranges 0 to infinity so this is necessarily a gamma function integral ok.

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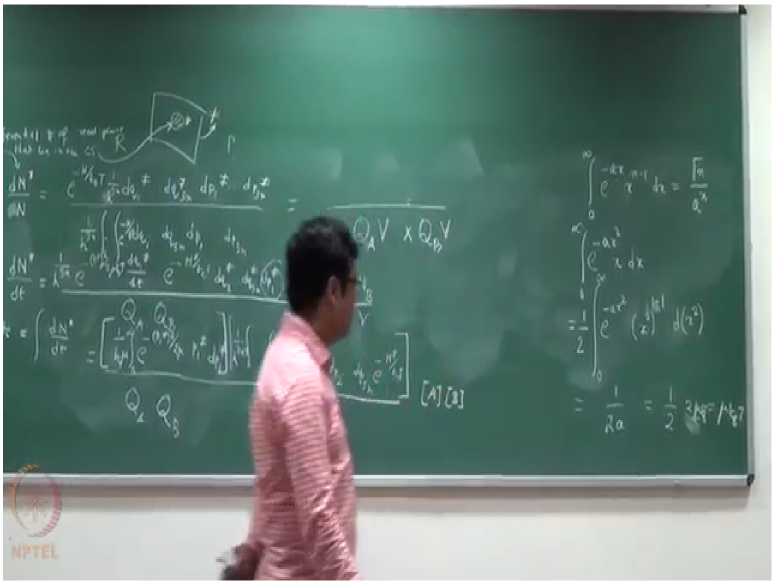

The gamma function integral if you remember which is something like e to the power minus ax x to the power n minus 1 dx that will be basically gamma n by a to the power n now how you connect it just look at it. So, here I have something like e to the power ax square this integration is something like e to the power minus ax square dx something like that this is the integration right. 0 to infinity because I see that there is the p square term and the variable is p now there was a sorry there was a x also something like that ok.

So, how to what is the (Refer Time: 39:24) the (Refer Time: 39:24) is the first look at here it is x square ok. So, what I am do is that I am going to task this one I am just make it as e to the power ax square , but this guy somewhere to make it as x square ok. Now the I can actually write it as d of x square now if I write it as a d of x square I have 2 raise dx right.

So, I have till something like half factor here that x already I (Refer Time: 39:59) here ok, but then what I have is x to the power 0 or basically I have x square to the power 0 the 0 is basically 1 minus 1 where is the integration.

Now, you can again make a changing variable that x square is now z now if x square is z the limits will be same 0 to infinity. So, it is now e to the power minus az, z to the power 1 minus 1 dz that is gamma n by a to the power n gamma n is 1 gamma n is gamma 1 by a to the power n a is basically also that whatever the constant so this will be nothing, but 1 by 2 a.

Student: (Refer Time: 40:53).

What was our a? A is basically this thing 1 over 2 so this will be nothing, but one over 2 into 2 mu right so what will have this mu ok. Now we see that this is just mu and this mu and this mu are cancelled ok. So, what I have is basically we did a mistake here, so you do not the Hamiltonian, but we did not write the kBT this will be P square by twice mu kBT.

Student: 0.

So, the here is twice mu kBT is equal to mu kBT clear so if I have mu calculating here I will what I will have this mu and this mu will be cancelled. So, if these two cancelled let us just write the rate once again rate for bimolecular reaction.

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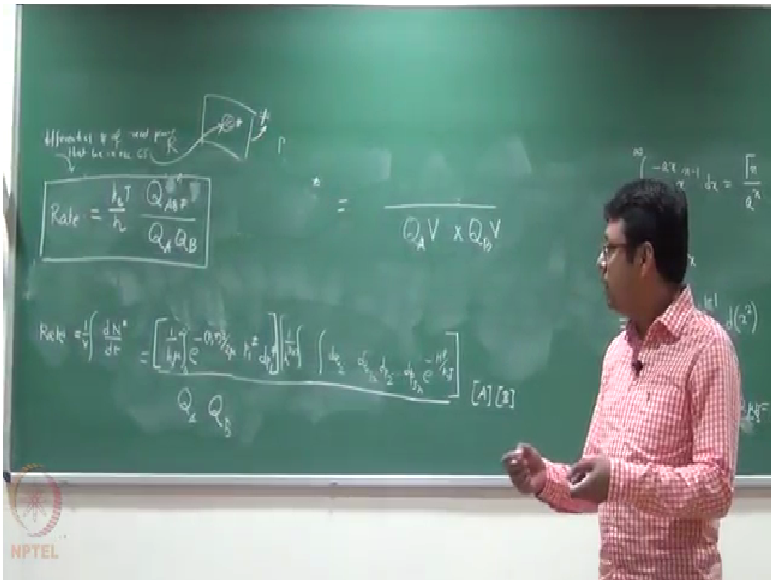

So, the rate will be nothing, but I have kBT by h right because the center term will give you kBT by h and then all these things, but all these things are nothing, but as I said this thing is giving me kBT by h it was kBT mu h is actually kBT mu and this mu is cancelling. So, I will have kBT by h and for this integration I am just writing it as h is also a partition function.

Student: (Refer Time: 42:47).

Clear but.

Student: (Refer Time: 42:49).

Which has 1 degree less.

Student: (Refer Time: 42:55).

Right which is.

Student: (Refer Time: 42:58).

I had approach the rate.

Student: (Refer Time: 43:09).

I should write it not this one, but per unit volume also because this is just a number rate is defined as the concentration. So, remember this is basically partition function time's volume and that volume and that volume cancelled.

So I am not writing it in the final form and then I will have QA QB all right this is exactly the same expression as I needs ok. Now what is the essence the essence here is that, then when I showed this is entirely classical beginners. Now what is the trick the trick is that I am thinking that I have in my phase base thinks are moving around the trajectories which are moving from reactive side to the product side, I am also taking there is a dividing surface which I called as a critical surface ok.

Now, I can calculate what are the number of trajectories which I am going to left to right per unit and per unit volume that is my way, but instead of calculating that way what I deal is that, I have just calculated what is the probability or the fraction of molecules which aligned in the divided surface and at what way they are crossing ok. That is what we clever the things, but as a result what we see here is a inherently number one this dynamics can be shown as a classical dynamics. Because this partition functions are classical partition function because h was just p square by twice mu all classical ok, but I get same expression.

Secondly it is inherently dynamical because I am considered it dynamics this is actually 1 degree of freedom which is crossing ok. But finally, I don't care because I have integrating out all the dynamics and I am getting the kinetical partition function without invoking any idea that there is a equilibrium between the transition state at the reactant, I need that equilibrium because I have to connect it through the partition function because there is a relationship between equilibrium constant and the partition function.

But here I did not actually consider anything I just say things are moving from left to right which is very much dynamical ok. And there I can also compute everything the partition function came only to calculate the number of states or the fraction of states.

Now, the transition state theory is that verses the dynamical theory dynamical theories the sense like where you actually do reaction dynamics is that here. Now it is the state counting problem why meaning it can actually just use a electronic structure theory if you calculate the partition function you are not solving any time dependent equation. Be it Newtonian be it Lagrangian be it Schrodinger equation the time already is in hand, but it got cancelled because kBT by h has the dimension of rate ok.

So, then you can just do electronic structure theories how h shi equal to e shi what are the density of states then need not calculate the partition function of A partition function of B partition function near the transition state. And if you can calculate the density of states, then you are done then you don't need to do any like dynamics as such only that h shi equal to e shi solution you will give you the dynamics itself because I have derived the equation ok.

Now, from here let us just see how to basically go to the unimolecular right the unimolecular we already discuss that there is a model which was like unimolecular reactions initially to the thinking that it happens due to radiation. If you both have like which gives you the radiation, then let us say that any reaction is happening in a container and any container has a background radiation thermal radiation, which is the background radiation.

But then there are lot of controversy and then people sure that radiation cannot do enough excitation which can cause breakage.

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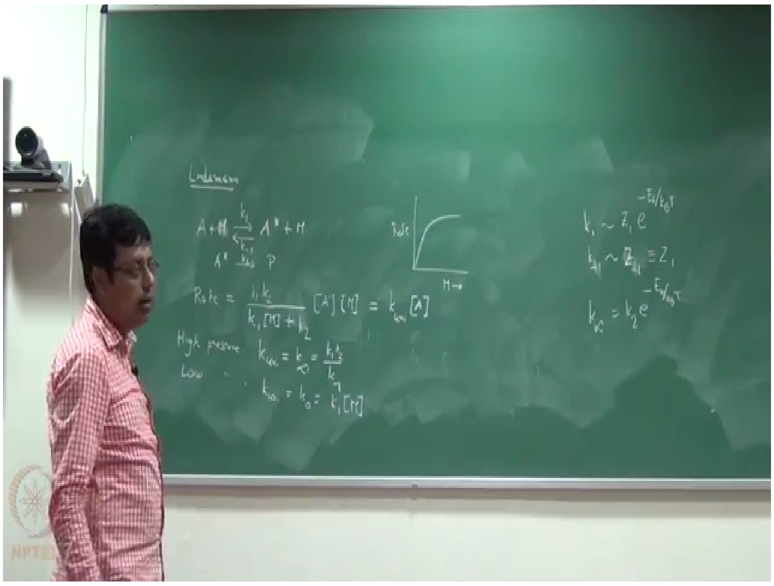

Then actually relevant propose that so there should be a bimolecular reaction that precedes the unimolecular reaction which is basically to product. But this m it is a second product which can be an a molecule which can be the walk of the container. And this due to this collision we have an energised molecule then like that deactivation collisional deactivation and once in a while this a star actually gives you a product.

So, the essential is that there is should a bimolecular collision that precedes the unimolecular reaction ok. So, I can have the rate constants k 1 k minus 1 and k 2 and this is the very straight forward thing like if I apply the either equilibrium approximation or the (Refer Time: 48:22) if I just consider there is a in first equilibrium the overall range. You can always write as something like k 1 k 2 divided by k minus 1 into m plus k.

Now this actually appears everywhere this kind of model like steady state approximation non-equilibrium everybody derive this so you always get this kind of equation ok. And suppose the now we can quickly see here if I have a high pressure limit because these initially were all done for the gas phase what will happen for the high pressure high pressure means actually the concentration of m is very high ok.

So, you can easily see that. So, before going to that we always write it as some like k unimolecular of A and can see in the high pressure limit what will be the k molecule. So, I will have m here so k of minus 1 k is much greater than k 2 so I have k 1 k 2 by k minus 1 and m is cancelled ok.

So, in the high pressure limit I will have k unimolecular which we write it basically as k infinity it is high pressure that is nothing, but k 1 k 2 by k minus 1 ok. And similarly I can also think about low pressure limit so the low pressure limit is something like k unimolecular which we write it as k 0 a low pressure means this term will be small. So, I have k 1 k 2 by k 2 k 2 will cancel so what I will have is k 1 into m ok.

So, these are basically the two limits of the unimolecular reactions and (Refer Time: 50:33) basically successfully all that at low pressure unit. If I just plot the rate constant versus the concentration at the species as you can see that at a very low pressure limit as you can see which one.

Student: (Refer Time: 50:52).

Yeah, but I have to set it a unimolecular thing I wrote a say for it so it is something into this thing and I am approximating that thing only so a I am not writing ok. So, now, the question is how you calculate these individual rate constant for unimolecular reaction.

Now there has been many theories now the first successful theory was basically now we can think like what will be the rate of a unimolecular reaction we can proceed with say bimolecular collision from your Maxwell Boltzmann distribution and then you calculate the collision theory ok. And then you can think that k 1 will be something like your emission frequency right, but not on collision will give you a star you can think that there will be some probability that I cross this energy then only I can actually get this ok.

But the deactivation part will be something like see deactivation does not need any like de it is a de energized pattern. So, basically I can write it as z minus 1, but z minus 1 and z plus 1 are same because polarity will reverse it is basically collision between A and m or A star versus m not it doesn't care it is a kinetic energy thing right. So, what is the total (Refer Time: 52:27) total is the temperature that A star is actually going to the internal edge. So, the deactivation or the activation does not matter, but for activation I definitely need to cross the barrier for deactivation the assumption is that you don't need to cross any barrier you can deactivate yes lose the energy ok.

And if you take the ratio k 1 by k 2 k k minus sorry this should be the k minus 1 ok. So, you will get basically an Boltzmann factor so the rate is nothing, but k 2 into the high pressure limit ok. So, this k infinity is nothing, but k 2 into e to the power minus e 0 by k b t, but which is not correct and people when plotted it e 0 you can get from erroneous parameters ok.

So but then when they plotted it they found that it doesn't match and it is a huge deviation now the question was why huge now then in the first thing what. So, this is the Lindeman hypothesis and then the next thing can next by significant modification ok.

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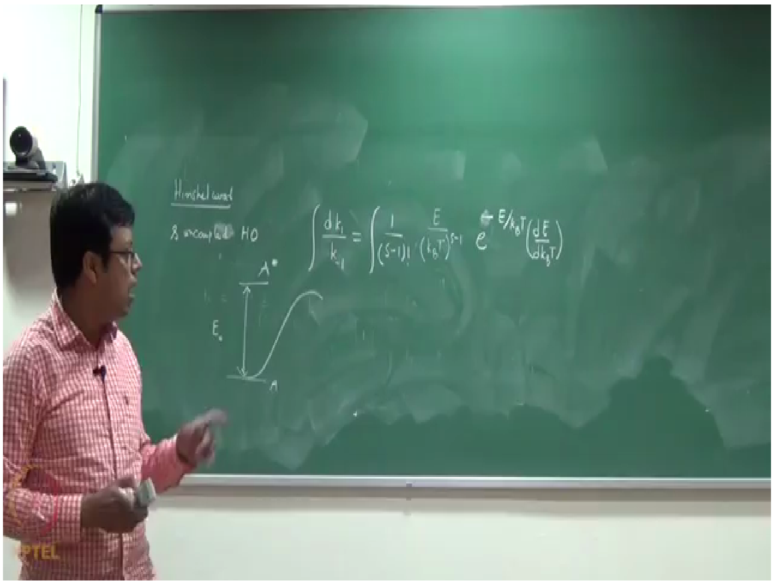

Was made by the American physicist chemist physical chemist Cyril Hinshelwood and Hinshelwood said fine what we say here is the kinetic energy ok. But in reality what is happening A star a molecule having high kinetic energy it is not the sufficient collision it should have enough internal degrees of freedom, what are the internal degrees of freedom vibration and rotation he considered only vibrations ok. And as a module of the molecule he said that there are some 3 N minus 6 or 3 N minus 5 vibration or degrees of freedom those vibration he said let us assume it to be harmonic oscillators ok.

So, I have basically s small s harmonic oscillators which are my system so there are some s uncoupled harmonic oscillator ok. And why uncoupled because I am just considering this to be very independent now this part will give an hand out when how to calculate this total like how to calculate the probability what we say it is uncoupled harmonic oscillator alright. So, what he said is that fine I am just write this over added thing again. If I just calculate the fraction this what is this fraction this fraction is a differential fraction of the molecules the probability at a molecules are getting energized ok.

And that according to him is basically I have suppose E 0 amounts of energy and what I am doing is that there is some reactant and product ok. So, all Hinshelwood say that suppose there is a star here after the collision and I have a here and this much energy suppose I am giving to the molecule. He ask this question how this energy it distributed among these s uncoupled harmonic oscillator that will be the most important thing you calculate ok.

How the internal degrees of freedom are getting this e 0 because if it goes to the transition it doesn't matter the molecule will just fly off until and unless it goes to the internal degrees of freedom then only the bond breaking or making happens that is the very simple thing, but this calculation we kind like show it later ok. So, it will give you something like 1 minus s 1 factorial and then E by kBT to the power s minus 1 and (Refer Time: 00:00) minus e by kBT so the book by (Refer Time: 57:21) or Henderson hasselbalch ok.

So, that has a bigger discussion how to calculate the density of state for n s unharmonic harmonic oscillator which are uncoupled because usually we do not solve the harmonic oscillator problem in the phase space and calculate ok. So, again the total probability will be something like this now here is the catch the catch here Hinshelwood said that fine look this is what this is what we have computed we have computed basically what is the fraction of the molecules how the energy is basically partitioned among the s harmonic degrees of freedom that is it ok. But necessary collision is that the reaction will happen if and only if ok.

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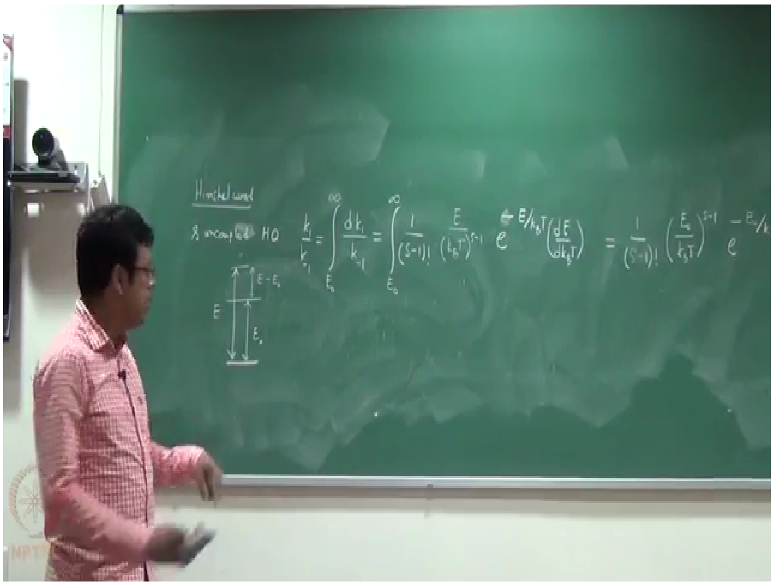

So, basically I am trying to calculate this molecule k 1 by k minus 1 I just cannot calculate over all the energies why because I need a minimum energy of the reaction you have I will not say reaction will not happen ok. So, then the integration will be something like this and you can actually make a substitution like you can we can show it how to do it. So, basically you write this thing suppose this is the total energy and then all I am saying is that I need a minimum energy E 0 then the energy other value for this harmonic oscillators is nothing, but E minus E 0 where E is basically fixed ok.

And then we can make a substitution and then we can actually solve this in detail I am not solving right now and if you solve it then you can show that this will be the something like 1 by s minus 1 capital here E 0 by kBT raise to the power s minus 1 and there I have E power minus E 0 by kBT that. Now what we have done here what Hinshelwood get is basically calculating this ratio energization divided by deenergzationi, but then that we do not do experimental or that we do not measure experimental right ok.

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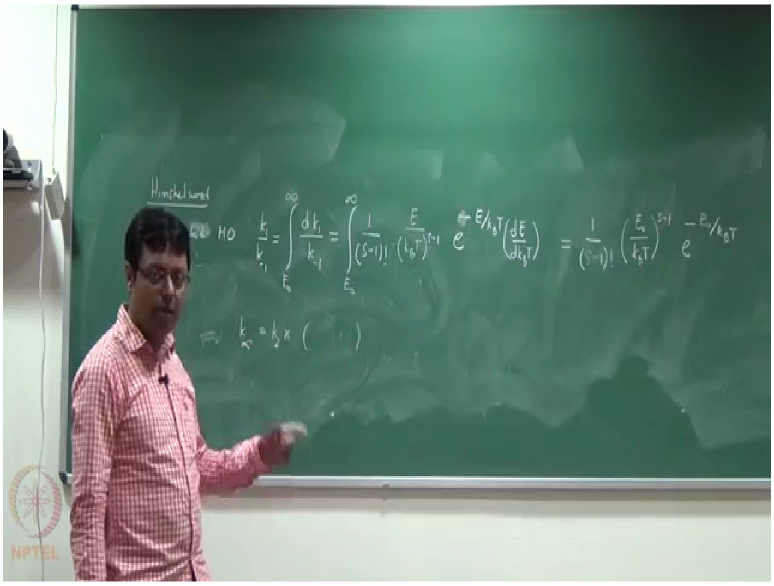

Measure experimental is something like say the high pressure causing which is nothing, but k 2 times this thing ok. Now, the question was you can calculate it for any molecule unimolecular reaction I know (Refer Time: 60:26) case I can actually do a (Refer Time: 60:28) analysis, I can get all the frequencies I know what is the number of (Refer Time: 60:34) case. I can calculate that threshold energy from the experiment and then I can calculate this factor it is not very difficult to calculate.

And then k 2 is basically nothing, but frequency of that vibration which is the (Refer Time: 60:50) vibration that will give my reaction if that only calculate then again there is a problem the problem was basically the form that it deviates from the experimental method by (Refer Time: 61:04) ok.

And then another group of basically concept came that was focussing how to calculate k 2 which means what Hinshelwood did Hinshelwood did a beautiful thing Hinshelwood take the first step how the energization happens which was correct. But once I have the a star how that A star is giving me reaction for that the other theories came ok. Now there are an systematic development for this thing I have just do that the RRKM theory.

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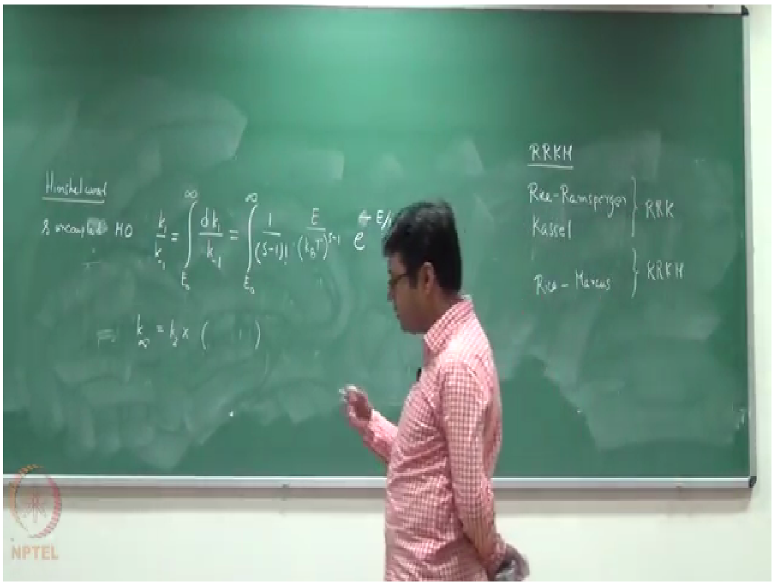

So, the RRKM is basically comes from rice Ramsperger ok, so this is actually (Refer Time: 61:58) rice (Refer Time: 62:00) rice and his (Refer Time: 62:00) Ramspergen actually gave a model which was also given at the same time by Kassel ok.

This is known as RRK theory and later on Rudy Marcus as a (Refer Time: 62:16) of (Refer Time: 62:17) rice bring this (Refer Time: 62:21) problem ok. And that is why it is known as RRKM theory. Now we will skip the systematic development it is very interesting though ok, but we will directly go to the RRKM what is basically the essence of the RRK model ok.

Now what is the essence and what basically Rudy Marcus said ok. Now when Rudy Marcus was doing I mean solving this problem in 1940s most likely that time already transition state theory was known wigners (Refer Time: 62:55) also, so he had in this mind very much like something like a concept of the transition state theory ok.

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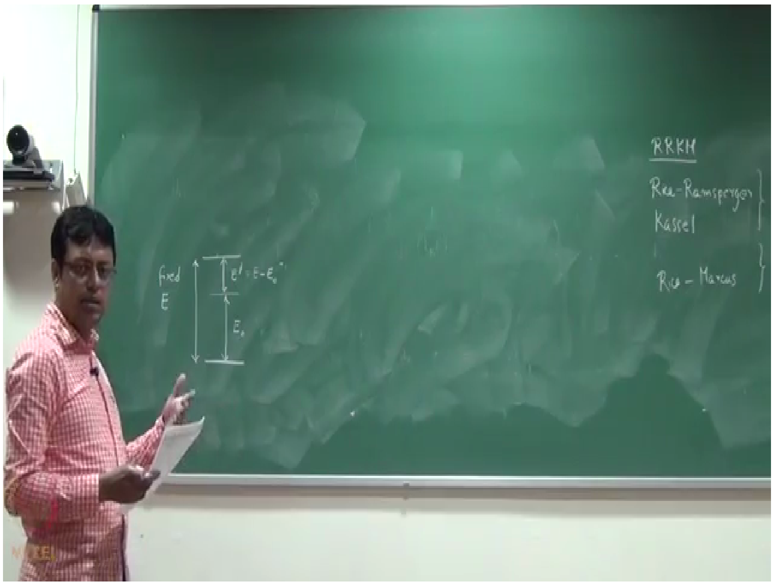

And then he said fine what is happening here let us think about it right I have again think about an energy ok. So, suppose my total energy is fixed now what I am solving right now is that I have some threshold energy same way like Hinshelwood was thinking ok. And this is the energy which is available to the node now this threshold energy again it is kind of for crossing the barrier and this energy actually I can write it as E dagger it is something like a transition state notation ok. So, E dagger will be nothing, but E minus E 0 ok. Now what he said is that fine all I have to find all I have to do in the transition states theory is that I can actually define a density of state or number of states.

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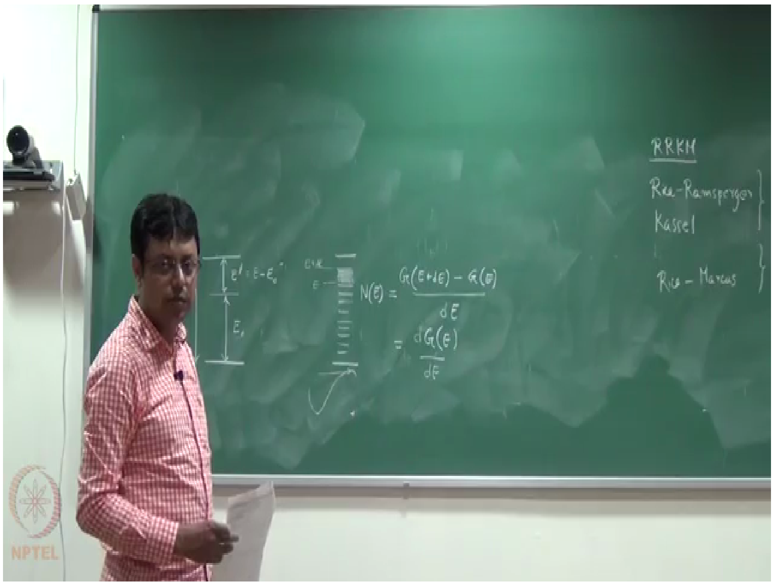

So, how what is the meaning of density of state suppose I have some states here now I can actually calculate what is the number of states between say E to E plus d E clear ok. So, that thing new thing basically the number of states at E plus d E minus number of states at E, now what will be the density of state density means it is a energy density per unit energy level, so if I just write it like this that I call it as a density of state.

Now in the limit that this d E is very small then I can use the differential one which means then I can actually write this is nothing, but d G and d E. When actually this is a trace bond doing these thing find continuous because until and unless it is continuous I cannot use a differentiation because it is a, for continuous variable ok. All the molecular energy levels are discrete to a kind of saying that for a particularly for a high energy for that is why actually you are crossing the (Refer Time: 65:46) ok.

So, your density of state of course, increases it is not a very bad assumption to begin with that if there will be a density of state collision where actually I have a continuous energy distribution ok. So, then this is the density of state expression now again I can actually calculate this number G the number of states per how many cross value that we will show how to calculate so that if we do it.

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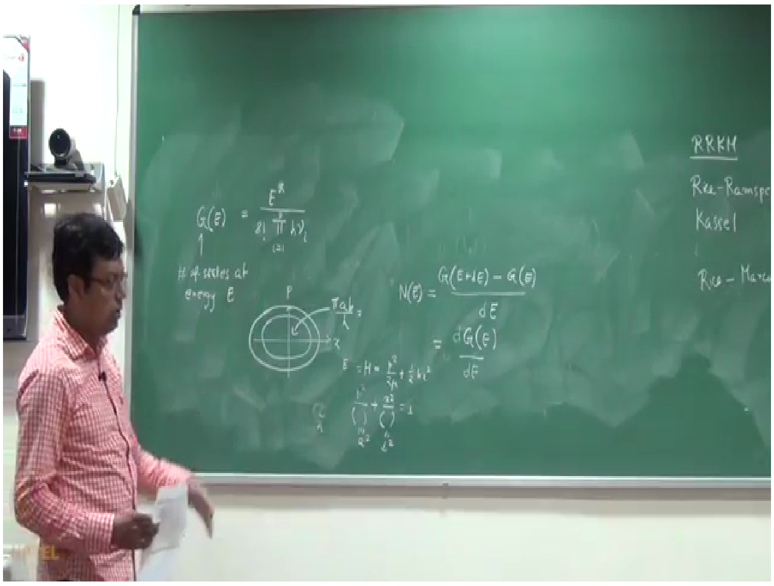

So, G basically means the number of states at energy E clear ok. So, for s uncoupled harmonic oscillator we can show that this number of states will be something like this. And so this kind is small s even if I do not write usually this be a small s where nu I for the vibrational degrees vibrational frequencies and s how many cross values I will have nu 1 nu 2 nu 3 all these things ok.

So, this is how you calculate now how you calculate it so it is some give you big hand out where you will see this for example, for ellipse ok. So, what is the equation of motion for an ellipse or a harmonic oscillator now I know that Hamiltonian means what P square by twice mu plus half k x square right clear or if the energy space suppose I am fixing the total energy. So, then actually I can write this equation as something like P square by some constant square plus x square divided by some constant square is equal to 1. So, that is equation of an ellipse where this is basically semi major or semi minor axis of the ellipse right.

So, in the phase space now how many cross values thing will look like this or a fixed energy if I increase the energy it will have another counter something like this. So, all we are doing is basically calculating these and then dividing by if I divide by h then I will get the number of states as simple as that ok, but now this has to be extended to s harmonic decrease of it not only just one got it. So, the number of states you can easily calculate ok, so I have basically this thing then you can easily calculate the phase space volume because you know a and you know b and the area of the ellipse is nothing, but pi a b ok.

So, here clear this is exponential if I write this equation like this this will be the area and this divided by h will give me the number of states for a one dimensional ellipse similarly we can actually do it for like s dimensional ellipse. So, that actually there are s different oscillators that will give you this thing clear e to the power s divided by all this thing alright.

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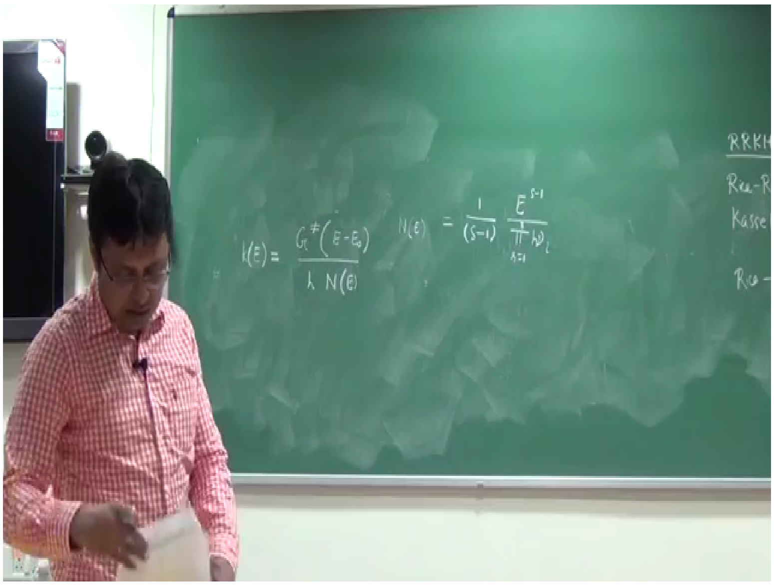

Now this is the number of states so what will be the density of state? Density of state is just you will take the derivative with respect to what? With respect to energy well. So, what I have is see here it is s so I will have s minus 1 ok.

So, I am just writing it first I have s minus 1 and then I will have E to the power s minus 1 divided by I have pi h nu I s equal to 1 (Refer Time: 70:25) ok. Now this is one thing, so if you remember that the rate constant which we did in the bimolecular reaction. So, if you remember that rate constant was something like if you remember correctly that that time you are considering that we have some number of states right divided by the total number of states because that is how we calculated it d n by d x star by n something like that.

So, in the RRK model actually you do it and once you do it we can show that for this rate constant will be nothing, but I have I have to calculate what is the number of states ok, which are lying above E 0 divided by this quantity. Now what is n? N is basically the density of state from the entire thing now let me just write it here so just a minute.

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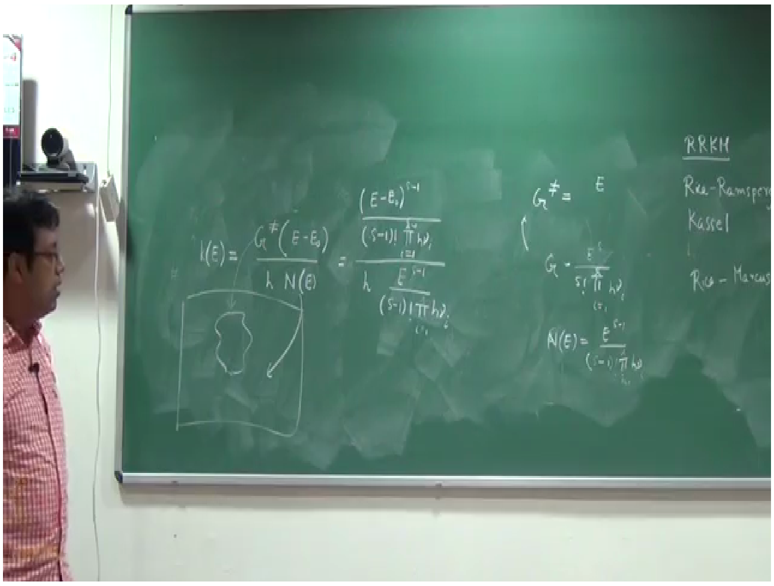

Now, I have the expression for G as E to the power s s factorial then I have basically N of E I have basically E to the power s minus 1 s minus 1 factorial h nu 1. (Refer Time: 72:35) Now think about it one I have written it is basically G dagger it is a same concept ok.

So, I have a radian in the phase space I want to calculate the number, but when I calculating the number is a thing the thing is that they said that one degree of freedom will be less always. When we calculate when you calculate one degree of freedom less meaning you have to isolate you have to write this thing as something like a for g dagger you have to write it something like one combination which is 1 E and 1 h nu that you take out and then you write the rest of ok.

So, G dagger means actually the number of states which has one particular degree of freedom less so this expression will be something like the similar expression. So, we can follow it so I have something like E minus E 0 now instead of s it will be s minus 1 why because there is (Refer Time: 73:52) numbers ok.

Here instead of s I have s minus 1 factorial and here the summation is also be I equal to 1 to s minus 1 divided by I have h and density also ok. Divided by I have h and then what I have the density of state expression I already shown it is E to the power s minus 1 divided by s minus 1 factorial pi h nu i; i equal to 1 to s. Now again think about it this corresponds to this region and this number of states corresponds to the entire region something like that ok.

So, now you can seen there is a h here this h and this h can be multiplied and then what happens is that (Refer Time: 75:00) in the denominator and numerator so taking of h right away ok. So, this expression will be reduced to something like it will be something like by here E minus E 0 divided by E to the power s minus 1 right.

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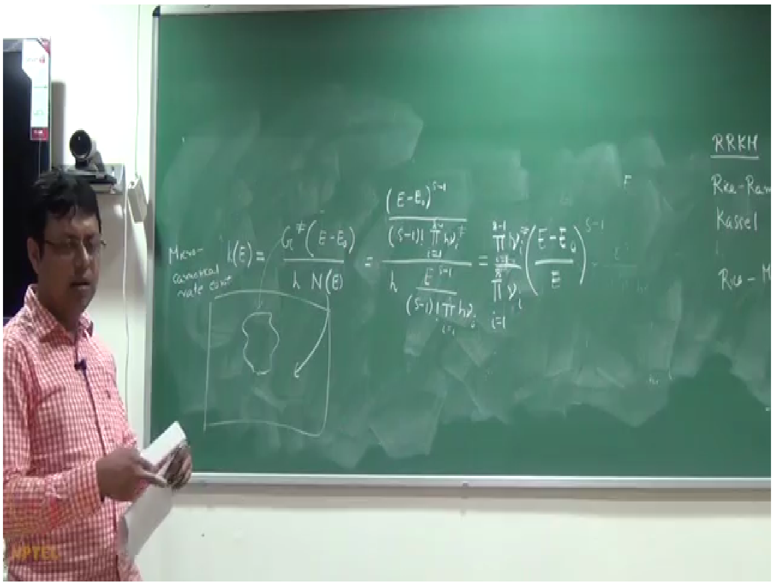

And then I have a interesting thing here pi nu I then this will be my dragger I divide it by I nu I will corresponds to s and s minus 1. Now what you mean by this think about it what I calculated the values like combined techniques right. And then how the pi comes, but if you remember that when you write the harmonic (Refer Time: 76:10) partition function all these h nu s get multiplied that gives the notation for (Refer Time: 76:15).

Now, what I am getting ultimately go back to here only that I have a frequency which frequency, which are the transition state prefers right. The molecule when it is excited that will have some frequency just slightly different these are actually be a dagger ok. But then one frequency is less that is why it is sum is good for (Refer Time: 76:40) s minus 1 denominator I have the frequency, which are the normal forms in the ground state like it is a overall thing it is not the dagger thing it is a entire thing that is why it is basically in the ratio of the probability ok.

But at the end of the day interesting thing if we look at here it is a numerator sorry denominator has one extra nu dimensionally this one now just cancel because these set of frequencies are different from this set of frequencies ok. And also I see that the number is one less, which means overall I have frequency inversed unit which is rate ok. But this rate is not (Refer Time: 77:21) apparent state it is for a rate per fixed energy, but you do not do the experiment at the fixed energy you do an experiments with the fixed temperature ok. So, this rate is known as actually micro canonical rate constant ok, so this is known as a micro canonical rate constant ok.

But from there we have to actually calculate k of T right now how do you calculate that k of T you just have to calculate this k of E ok. What is it that if I have a fixed energy which is E the energy of the system what will be the rate times I have to also calculate what is the probability of having the energy E for a given temperature and then integrate over the entire thing and then I will get the rate constant ok.

That is what basically is the essence of the Markovs theory ok but how I arrive at it I will skip it again because this needs a lot of mathematic, but essentially as you can see this will be still the ratio of the states in some sense.

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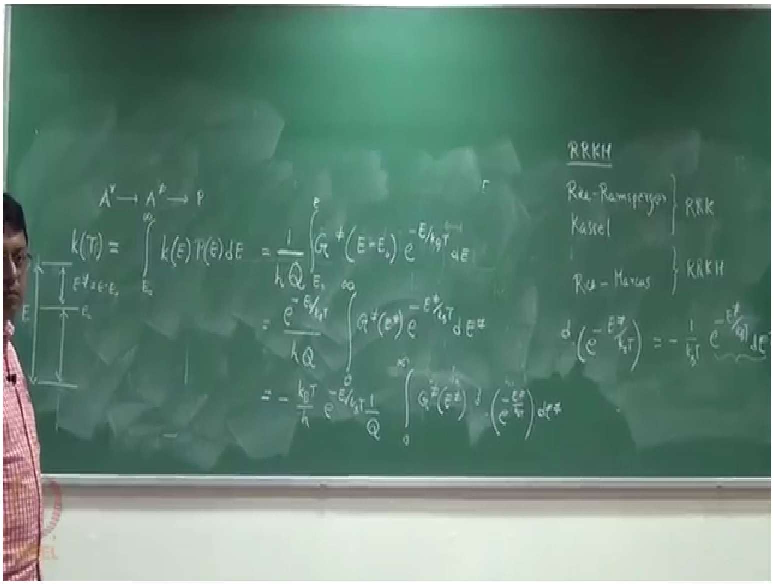

Now, so what Markov said is basically the similar thing like I have something that energised molecule going to product, but then beside that if it is something to go into an activated form that is the essence of Markovs theorem ok. The m modification of markovs the earlier expression which is shown is mainly due to the RRK version ok. Now how do you get k of T you basically get your, I can I always can calculate k of E ok, but then I have to say what is the probability that I have the energy E ok. And then I have to integrate over all possible values that is the essence ok, but then remember this has not the volume it has 0 because the condition is that you should have your minimum energy easy again let me just draw the picture ok.

This is what is happening this is the total amount of energy x right and then I said I need minimum E 0 to cross right. So, the condition state basically gets a share which is E minus E 0 clear what can be the total energy if I reduce it reduce it reduce it if I go up to E 0 it will just happen the reaction if I go below no reaction form. So, I can have E like so this is for fixed E, but now for fixed temperature this E will also change that is what I have said ok. Now E will change in such a manner that it cannot be below E 0 if it is (Refer Time: 80:46) then this line go to 0 ok, but E can go to infinity then this line also can go to 0 ok, but that 1 limit has to be 0 ok.

Now, from going from a micro canonical to canonical means now I am saying that a E itself is y at a fixed temperature, but again it cannot be base line. So, because then this guy is in (Refer Time: 81:10) is moving now let me say is that final. So, I have basically in the centre of like the number of states were I can write it as something like the number of states which are I think energy is more than E 0.

This is exactly your transition state angle expression it will be (Refer Time: 81:46) time wrote it right basically the partition function one, but right now actually when followed density of sorry basically these G dagger ok. And what was our e expression remember we have g dagger divided by h n right what was n? N is basically the total number of states right. Now if you remember, but did the density of states basically now that thing you can always write ok.

Now, if you think that I am just writing it like this and what was the k E expression k E expression was basically G dagger divided by h n right, but n is basically the density of states which you can connect through partition function we are not showing it here ok. We are just saying that fine I will have an expression something like this ok, now this is again this is the micro canonical part and the probability it is here just suppose my probability and all I am going to do is to integrate between E 0 and E ok.

If in this picture enough now I am writing here also now the question is fine then in a state where how I solve it ok. Now do a change in variable what is the change in variable look at here if it is 0 space I can actually write at E is also fixed for the micro canonical thing ok. But I can actually instead of writing it as like E I can actually interchange the variable and see there ok. So, means this total energy E is basically is E 0 plus E dagger now E 0 is a constant so I can (Refer Time: 83:59) will take out it out of a integral clear ok.

So, what I am saying here I put write this expression a E power minus E 0 by kBT by h q then these guy think about it E minus E 0 is what dagger ok. So, this is nothing, but G dagger of E dagger what is this guy is basically E to the power minus E dagger by kBT what is your d E dagger d E d E is nothing, but E dagger minus d plus E E 0 but E 0 is a constant so I the change in variable only resultant if we taking out the factors E to the power E 0 by kBT ok.

But now if that one limit is E 0 what is the probability for E dagger if the probability is E 0 E 0 minus E 0 E z apparently E was infinity, infinity minus E 0 that is infinity. So, now, I have actually 0 to infinity and I have E 0 still it is a kind of what it is saying, it is basically saying I have a E to the power minus E 0 by kBT some h some Q ok.

But look at it I have basically something like G dagger which is basically the number of states in the transition angle which has energy E dagger and I am adding this in that. So, think about it if the probability varies this thing also varies because this is varies now I have actually this is a variable now this will also that. So, I have change the variable from E to E dagger that is it because E 0 is a constant now this looks pretty odd like pretty odd expression at this point right.

It is again go like partition function and all those things now let us see how to basically cleverly to observe it ok. Now look at it carefully now what is your this thing like I have monotonically (Refer Time: 86:24) like exponential thing let me just write it like this.

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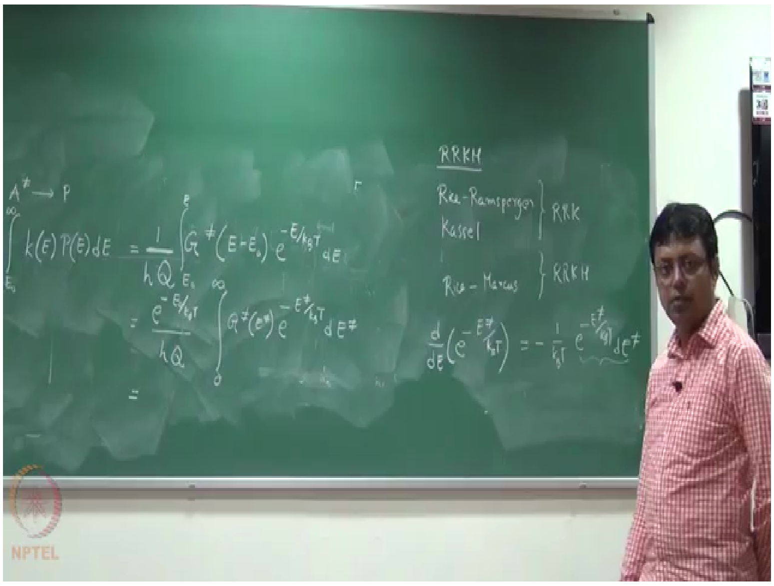

First let me what is this term say I have actually two variables u v d x. So, I have to integrate by parts because this is also function of on a G because density of states of course, changes like number of states of course, changes as a function of energy ok.

Also I have this Boltzmann factor as a function of E dagger ok, so I have to do integration by parts ok, but I am just playing a trick the trick is that fine the integration parts if you remember that I have to do u integral v x and that right and then there is a derivative part. So, one is this one if I do it so this will be minus 1 over kBT right and I have e to the power minus E dagger by kBT E dagger right.

So, these guy and could have written as this multiplied by minus kBT why I am doing it because see now if I have this thing I have a kBT by h factor here connecting to your like by molecular connections that , but there is a minus sign. So, there is a minus sign of kBT by h, but now I taken care of the kBT by h term I have also taken care of the e to the power minus E 0 by kBT term which also appears time in (Refer Time: 88:15) I also have 1 over q which is there.

So, that thing should be q q dagger basically how that is a question ok, so what I have now is integral 0 to infinity this G dagger and E dagger and d d E dagger sorry it is E dagger of E to the power minus E dagger by kBT clear. And that should I have write it like this d of yes a differentiate basically clear up to this part right, now see this is actually easier because I can actually use it as a first function because first function is basically integral of that right. So, if I integrate it will be the same thing so let us just write it so I have this factor ok.

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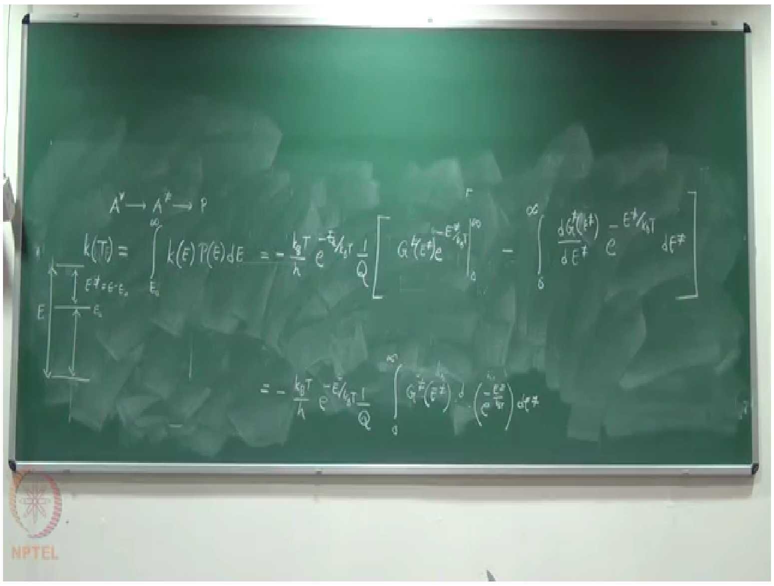

Minus kBT by h e to the power minus E a by kBT 1 by Q now whereas, ok. So, what I am saying here is u v d x ok, so u integral of v d x so u is basically this integral of this is the same thing ok. So, that I have E is G dagger it is a function of E dagger E to the power minus E dagger by kBT if I am write it between the limit 0 to infinity right.

And then what I have is minus integral now what I have right this derivative of this right and then ok. So, I am I am just writing the first let me repeat it and then integral of this thing which will give you e to the power minus and then clear ok.

Just integration by parts what will get if I have 0 if I have infinity here ok, so e to the power minus infinity by kBT that is here if I have 0 here the density of states which we can see which means this part is 0 ok, what about the second part these following by definition is the density of states.

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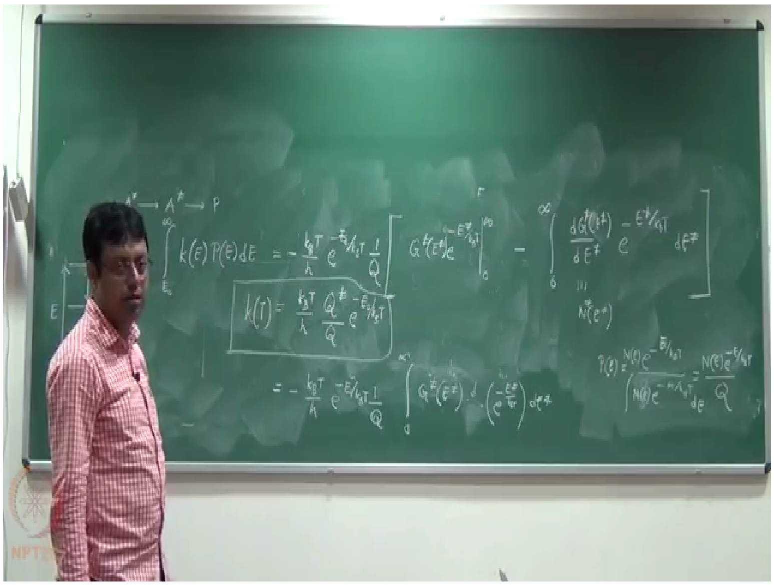

It is nothing, but N e dagger right because derivative with respect to state is basically density of state ok. And density of states what is the partition function basically partition function you know that is write it as a the probability solution by e to the power minus h by kBT and then the we have.

Now, this is if I sum over the states if I sum over the states if I sum over the neighbour. So, here I add number of this is nothing, but this thing right which is that Q clear. That is why that N e to Q we wrote it as that is why we as wrote it as h Q combination this is the definition of the probability ok.

Now think about it like then I know that by the definition what is N e E to the power minus kBT and the integration of that then it is nothing, but your partition function itself that is a function itself is N e; E to the power minus e kBT but what partition function it is or T transitions state. So, this is basically E dagger, but then I have many to (Refer Time: 93:59) because it was a u integral of e minus that minus and that minus now cancels. So, what will have is kBT by h if I write that 3 as Q dagger by Q E to the power minus E 0 by kBT ok.

So, that is basically the Markovs theory so basically Markov showed that I have the same Eigen equation kind of expression which were react for the bimolecular reaction in a very, very different way clear. And, but again we actually skipped many steps in showing it because we showed that there is a all this harmonic constant error calculations we did not showed explicitly.

But what we can show here is that this probability if you remember know any the will be is nothing, but (Refer Time: 95:01) by the divided by the probability which is the (Refer Time: 95:05) function if I bring by level then levels can be degenerate. So, our level moves energy e can have N state that is basically the meaning of density of states and then this is nothing, but E power minus E like this. So, Q by definition is basical state times the Boltzmann factor and then if we just integrate over the all the energies ok.

And here if you see that derivative is nothing, but the density of states is multiplied by Boltzmann factor and this has to be the partition function, but what partition function because this was only the dagger thing which is above the E 0 ok. And then basically Markov shown the canonical range reaction right is equal term to the bimolecular transition set or here it is ok. So but there is a clear difference there I have Q A Q B has to be because actually there was A and B giving me product A actually starting from A starts itself ok.

And then he showed that basically transition actually is also true for unimolecular reaction. So, Markov is basically gave the transition state theory version which is basically the wigners way the diagonatical way version of unimolecular reaction ok. And he said that it is basically the same expression ok, but in a very different way because originally if you remember the why you were writing it is its very, very different like s uncoupled oscillator and that way right, but at the end of the day you get the same expression alright so we just stop here