Advanced Chemical Thermodynamics & Kinetics
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Lecture – 29
Unimolecular reaction 0I

So, we have seen for a bimolecular reaction the rate constant can be derived according to the transition state theory for bimolecular reaction.

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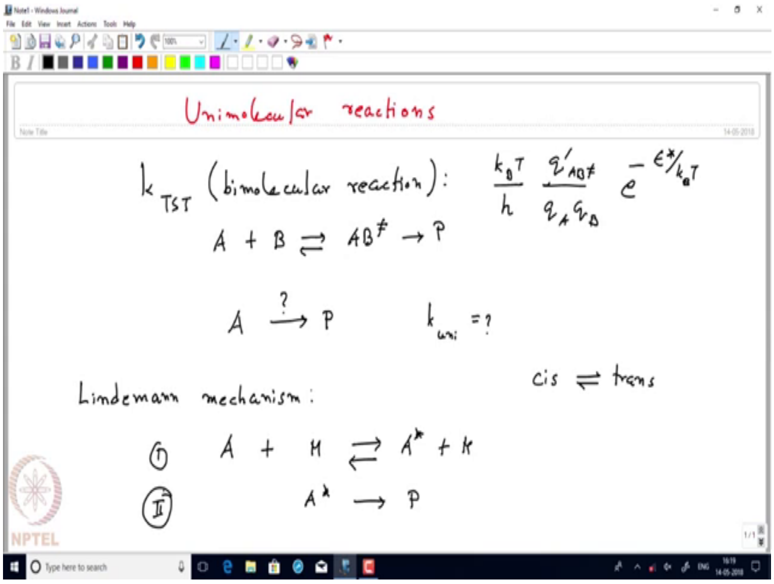

Unimolecular reactions

k_{TST} (bimolecular reaction): $\frac{k_B T}{h} \frac{q'_{AB^\neq}}{q_A q_B} e^{-\epsilon^*/k_B T}$

$A + B \rightleftarrows AB^\neq \rightarrow P$

$A \xrightarrow{?} P$ $\quad k_{uni} = ?$

$cis \rightleftarrows trans$

Lindemann mechanism:

(I) $A + M \rightleftarrows A^* + M$

(II) $A^* \longrightarrow P$

And that we found as if you remember that it is a bimolecular elementary reaction something like A plus B, and the assumption was that we have a transition state in between and that is giving the product. And then the rate constant was found using the adding equation was k B T by h and th en I have the ratio of the partition function of AB dagger divided by A and B. I was using probably small q notation, q A, q B. And then this has 1 degree of freedom less that is why we wrote it as a prime and e to the power minus E star by k B T, where E star is the differences between the 0 point energies of the reactants and the transition state.

Now, today we will see what are the treatments for unimolecular reaction. Now, there are many reaction unimolecular, again it is a unimolecular elementary reaction, and there are many theories to explain the unimolecular reactions. And there what is a unimolecular reaction in that sense? So, basically I will have one particular species going into the product, and we are I mean in a process to understand how one can write the rate constant for this unimolecular reaction.

Now, if you think that we already studied this Lindemann hypothesis I am going to repeat here once again. So, that we understand what are the drawbacks in the Lindemann model. Now, Lindemann propose that for any unimolecular reaction there is a bimolecular collision that precedes the unimolecular reaction. So, that is known as a Lindemann mechanism. Sometimes it is called Lindemann christens and mechanism, but we will just call it as a Lindemann mechanism or Lindemann hypothesis or Lindemann model.

So, Lindemann said that for any unimolecular reaction you will have a coalition of the molecule with something some other gas molecule, this M can also be the wall of the container and then you first form an energized molecule. And then this energist molecule subsequently gives rise to the product. Now, for unimolecular reaction there are many theories. For example, there were people hypothesized initially that the radiation or the blackbody radiation from the wall of the container actually causes the unimolecular reactions to happen, because the question was if a molecule is there what is the process of activation first because it has to cross certain energy barrier for the reaction to occur.

Now, one of the I mean theories or one of the examples of unimolecular reaction very nice example is cis trans isomerization. Now, here cis goes to trans and at depending on the system trans can also give you back the cis isomer. And these are actually called true unimolecular reaction in the sense that, you have really one particular molecule and it is giving you the another particular molecule in this case the molecules are isomers.

Now, the question is if we have a two process. So, I have a bimolecular process, so and then which is followed by a true unimolecular process, how one can write the rate constant and that already we have seen or in many cases. So, you will use the steady state approximation here; and using the steady state approximation for the intermediate.

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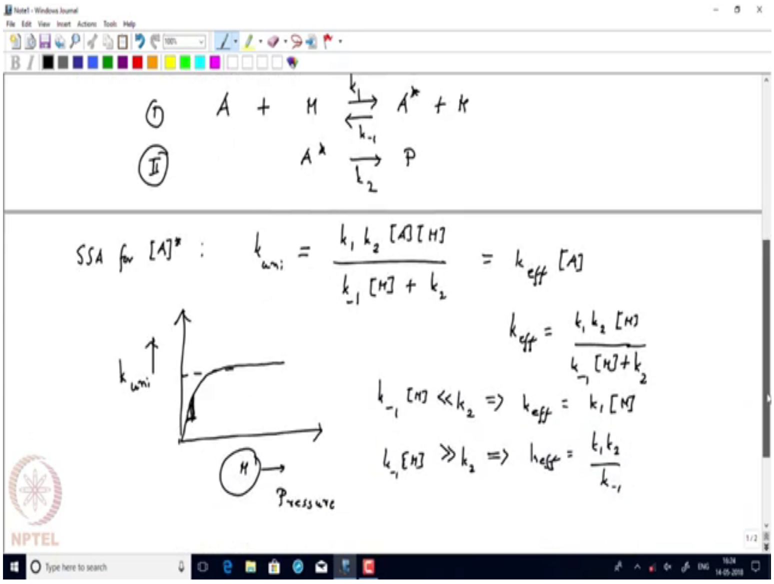

(I) $A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$

(II) $A^* \xrightarrow[k_2]{} P$

SSA for $[A]^*$: $k_{uni} = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2} = k_{eff}[A]$

$k_{eff} = \frac{k_1 k_2 [M]}{k_{-1}[M] + k_2}$

$k_{-1}[M] \ll k_2 \Rightarrow k_{eff} = k_1 [M]$

$k_{-1}[M] \gg k_2 \Rightarrow k_{eff} = \frac{k_1 k_2}{k_{-1}}$

So, the intermediate here is this energized molecule for the intermediate concentration. Then we can say that the rate of the unimolecular reaction overall rate that we have again derived when we will discuss the reaction mechanism, and you can actually go back and have a look at those lectures.

So, that will be nothing but equal to k 1 into k 2 times A into M divided by k 1 it will be k minus 1 not k 1 k 1 into M plus k 2. So, then you what people figured out is that they actually plotted these unimolecular rate as a function of pressure. Now, pressure of what? You can actually think of the pressure of the second body M.

Now, you can actually have inert gases also for this reaction the M can be actually some other gas molecule, and then you study the reaction and then experimentally people found the curve looks like something like this. So, at a very low pressure region you can see that it is basically the rate constant itself a unimolecular is actually a first it depends first order with respect to M, and then at a very very high pressure you will have that the apparent rate constant which we can write it as the apparent rate constant as k effective times M. So, this is one way of writing it. I will just write it as like this k effective into a where k effective is this entire term. So, k effective is nothing but k 1 into k 2 times M divided by k minus 1 into M plus k 2.

Now, the question is this is an effective again effective rate constant and it will have it is high pressure and low pressure limit. And then is as is apparent from this equation that if you have in the low pressure region, so you can think that the concentration of M will be much small. So, k minus 1 into M that term will be much smaller than k 2. So, what you will have is that the effective rate constant will be something like k 1 into M. So, that is the linear dependence in the low pressure region. And in a very high pressure region will have the other constraint that the k effective will now be, so basically in that case k 2 is much smaller than k minus 1 into M and then what you have is so I will ignore this other term k 2 and then the M actually cancels. So, then you will have k 1 k 2 by k minus 1 which is a constant and that is why you see a flat line. So, it does not change with pressure, pressure the total pressure.

Now, again M can be A itself, M M can be something else and can become some other gas also. So, if it is actually some other gas or the A itself, then I can actually represent the concentration of M as just pressure. So, this x axis is nothing but some textbook actually write it as just pressure. So, this is basically the unimolecular reaction kinetics at a very high and very low pressure regime.

Now, you see that what is the physical significance here is that what Lindemann hypothesis says is that for any unimolecular reaction, the activation is by collision activation is not by some thermal blackbody radiation from the surrounding because that is not good enough to actually excite a molecule close to the dissociation limit. So, that some bond breaks and some rearrangement happens and then it gives rise to another product. So, collision is necessary.

And the second thing here is that whenever you have the collosion you remember that from collision theory you can think that if the; a process of energization is happening. So, that rate constant for energization in this case is this first step, where this forward step. So, you are having an energization and then you are having a deenergization or deactivation. And then in the second step what you have is that the energized molecule actually gives you the product.

Now, think about it like if I have a small pressure, if I am working in the small pressure limit. So, the say there collision is happening and some I produce some a star molecules, but it did not these a star molecules have a little chance to get deactivated by collision again. Because the number of collisions are less in the low pressure region so whatever collision is happening and if the collision actually results in formation of a star. So those esters will actually give you product and that is why you are having the with increase in pressure. We are having actually an increase in the collisional activation or energization, the very first step in the in the in that equilibrium, the forward step in that equilibrium.

But if I actually increase the pressure too much then what will happen? This a star molecules will also I mean collide among themselves and as well as with other molecules and they get to collisionally deactivated. So, then the rate will actually get saturated, and because the deactivation will take part and then you will have something like a steady state like expression, not steady state like the equilibrium approximation like step. And we discussed about it that the rate of deactivation or the you have to actually remove the intermediate very quickly then actually you can get these steady state approximation hypothesis.

So, there it is a similar concept here. So, here actually I am talking about in the language of deactivation. And then if k 2 is much higher than the rate of actually deactivation is much higher than the rate of product formation which will be the case for the high pressure limit. Because if you remember that the product formation does not depend on the collision, because product formation is only the second step this step. And then in the high pressure limit the collision will happen and it will be activate.

Now, the question is the, this entire thing we only talked about the kinetic energy or the translational kinetic energy contribution. So, molecules are colliding and that is the entire source of activation of these energies.

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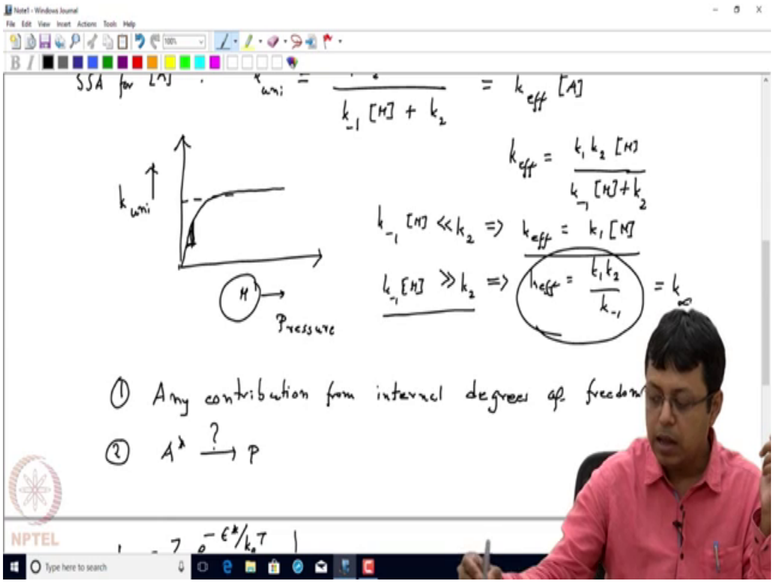
SSA for [A*] : $r_{uni} = \frac{}{k_{-1}[M] + k_2} = k_{eff}[A]$

$$k_{eff} = \frac{k_1 k_2 [M]}{k_{-1}[M] + k_2}$$

$k_{-1}[M] \ll k_2 \Rightarrow k_{eff} = k_1[M]$

$k_{-1}[M] \gg k_2 \Rightarrow \boxed{k_{eff} = \frac{k_1 k_2}{k_{-1}}} = k_\infty$

① Any contribution from internal degrees of freedom

② $A^* \xrightarrow{?} P$

$k = Z e^{-\epsilon^*/k_BT}$

Now the question is there any contribution from internal degrees of freedom. So, that is one of the biggest question, contribution from internal degrees of freedom. Internal degrees of freedom by that I mean that if we considered some say internal vibrational degree of freedom is it important to consider for this unimolecular reaction to happen.

Secondly, this mechanism whatever we talked it sheds no light on how this process actually happens how a star is going into product that dynamics or understanding about this thing is actually occurring that is not known. Only thing at the Lindemann hypothesis or Lindemann model provides is to tell, is to tell you that how these reactions are happening how this how this collisional activation is happening how the a star molecules are formed.

Now, this problems are subsequently tackled by many other scientists and many great people in the area of chemical physics actually contributed to this topic and then they said that this entire hypothesis we can or enter theorem we can think that fine these a star molecules are getting activated, but collision can give you an energized activation. So, let us first try to understand or try to write down what will be the frequencies of this collision k 1 and what will be the frequencies of this deactivation.

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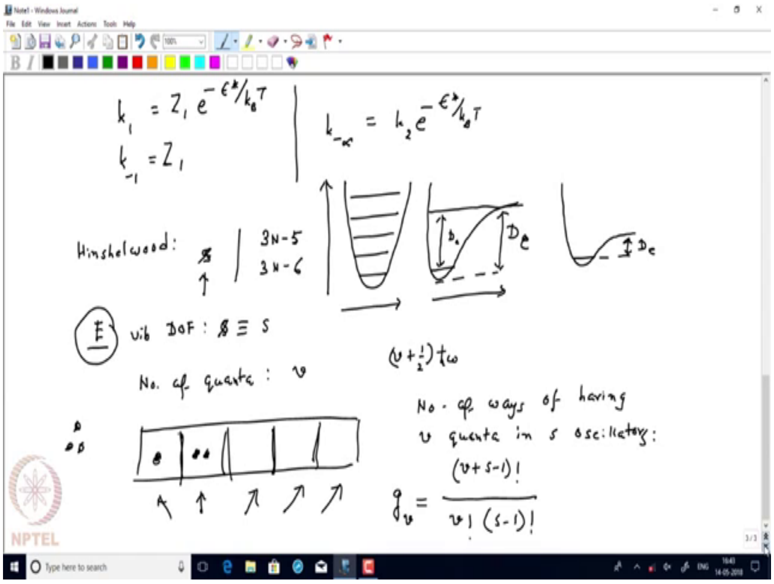

$k_1 = Z_1 e^{-\epsilon^*/k_BT}$

$k_{-1} = Z_1$

$k_{-\infty} = k_2 e^{-\epsilon^*/k_BT}$

Hinshelwood: ~~s~~ | 3N-5, 3N-6

E vib DOF : ~~s~~ ≡ s

No. of quanta : v

$(v+\frac{1}{2})\hbar\omega$

No. of ways of having v quanta in s oscillators:

$$g_v = \frac{(v+s-1)!}{v!\,(s-1)!}$$

Now for deactivation, you do not do not need any energy barrier because it is already some energized molecules are there and with collision they will deactivate. So, I can say that this deactivation rate is nothing but the collision frequency itself. So, I am writing it as Z 1 in the sense that this one denotes that we have the collision between same types of molecules, but it is not necessary that we have to write it as Z 1.

And secondly, this k 1 step it will also become dependent be dependent on the call number of collisions. But within certain energy criteria and we know that from collision theory, that we can actually calculate it in a simple with simple collision theory that we can if we say that there is an some threshold energy which is suppose a star, and we can say that the number of collision that is giving successful reaction is something like Z 1 the total number of collision into that probability which is nothing but a Boltzmann factor.

So, together I can say that in the very high pressure limit of unimolecular reaction which we wrote it like this, and sometimes we wrote it as k infinity, infinity in the sense that the pressure is in a very very high pressure limit. And that expression for this k infinity which is the ratio of k 1 by k minus 1 into k 2 so that becomes something like k 2 into e to the power minus E star by k B t that is what Lindemann hypothesis is.

Now, then came another model which was put forward by show Shelwood Hinshelwood. And Shelwood Hinshelwood proposed now that internal degrees of freedom are also very very important. Now, what is Hinshelwood's proposal is that, ok, fine.

So, what are this internal degrees of freedom and what are how we can model these vibrations? Now, these vibrations supposing you have if you have a linear molecule already we said that there will be some 3N minus 5 degrees of vibrational freedom for non-linear molecule there will be 3N minus 6 vibrational degrees of freedom, where N is the number of atoms in the molecule. Now, this all these vibrational motions or all these vibrational oscillator; I mean you can actually think that this vibrational motion are very much harmonic in nature.

Now, truly you cannot actually have any harmonic motion because a harmonic oscillator if you keep on putting energy. So, the energy will actually keep on increasing, and if the bond behaves like an harmonic oscillator it will never break. So, in order for the bond to break it has to be an harmonic something like that. So, that if I actually reach this much energy I see that the potential is not actually a bound potential and it should now break.

So, in this axis I am plotting the energy and this axis I am plotting the equilibrium bond distance and that we already discuss that if I excite I mean give this much amount of energy that we call as D 0, its D e sorry and if I consider the actual energy which is calculated from the 0 quantity that is known as a D 0. So, that amount of energy if I put then the bond will break.

Now, in a molecule you might have many different vibrations, of course, there are many different vibrations, and you can have actually different bonds and one of them might be very weak. Meaning in the sense that suppose the way I have drawn it, so this is for one particular bond, but another bond can be very very weak for which the actual dissociation energy which you need could be much much smaller. So, the idea is that when you actually energize a molecule which has many bonds or many vibrational degrees of freedom then first the energy gets a randomized among the all vibrational modes and then the weakest one breaks, and that is that will form our I mean the starting point for the next level of I mean theory which is known as the RRK theory.

But before that what we are discussing, right now the Hinshelwood mechanism that also basically provided the necessary concept for developing the RRK theorem. But Hinshelwood said that let us we know that this is actually an unharmonic problem, unharmonic oscillators every chemical bond have to break and then it must it cannot be an harmonic cannot be modeled as an harmonic oscillator. But with some approximation we can say that for the sake of I mean calculation because it can actually easily find out many interesting statistical properties for an harmonic oscillator. So, you can actually make this harmonic approximation.

And then Hinshelwood said that let us think about this problem that I have actually as fixed amount of energy and which is stored in the eastern molecule. And then the question which I am asking is that how this total energy which is suppose have some fixed amount of energy let me call it as say E, where E is a fixed amount of energy how that energy is partitioned among these different modes. Because when do to coalition I am actually activating a molecule E star. The activation means actually the al the energy does not go into its translational degree of freedom, because if it goes into translational degree of freedom nothing will happen only the energized molecule will move at a faster speed, but in order for this a star molecule to break this energy should be transferred or channel to it is vibrational or the internal degrees of freedom.

So, the question is if I have a given amount of energy in the in the molecule and how this energy is partitioned among all these 3N minus 5 or 3N minus 6 degrees of freedom. And let us call this number or how many vibrations are present I am just writing it as s. So, I have actually s vibrational degrees of freedom. So, degree of freedom or the vibrational degrees of freedom is s, it is actually small s we can write it as like this, but I am writing it as like this it is not capital s.

Now, now for harmonic oscillator you can actually talk in terms of the interest instead of the total energy, I can actually talk in terms of say what are the number of quantas. Let us say for example, if I have 10 quanta in an particular vibration. So, the total energy will be 10 plus half h bar omega 10 plus half h nu something like that.

So, suppose I have number of quanta is I am writing it as say v, because v is typically the symbol which we use for the harmonic oscillator I mean energy is the quantum number. So, v plus half h bar omega that is how you write it. So, that is what I am just writing it as v. So, suppose I have total number of quanta is v and total vibrational degrees of freedom is s. Now, the question is how many different ways I can put this v quanta in s harmonic oscillator. Now, each of this harmonic oscillator has its own natural frequencies, meaning if they represent some kind of bond or some combination vibration something like we talked about water. Say for example, this it has two bonds, but instead of visualizing it as that the bonds are vibrating locally. You can actually think about a global motion which is known as the normal mode vibration of the entire molecule, and you talk about the symmetric and asymmetric vibrations.

Now, at this problem you can actually solve statistically and then you can think and it very very interesting way. Now, suppose I have I am giving you a very simple example first suppose I have 5 I mean rooms, and then I am putting some balls in these 5 rooms. Suppose I have 3 balls and these 3 balls I can I am ask to put actually in these 5 different rooms. I can put it in many ways like, I can put these 3 balls like this in one particular room because there is no such biasness that I cannot put more than one, more than one ball in one particular room meaning I can there is no such biasness that I cannot put all the v quantities in the one particular oscillator.

So, this is related to something known as the if you have studied this quantum services this is exactly how we can derive the Bose Einstein statistics as opposed to the other statistics which is known as the Fermi Dirac statistics. And so, there the difference is that in when you derive the Fermi Dirac statistics you have to actually you can put only one ball in one of the rooms because of Pauli exclusion principle, and Fermi Dirac statistics are obeyed by Fermions and which says that it basically comes from that anti semitrization principle that you cannot put more than one particle in a given state, electronic state.

Now, in this case we have that relaxation we can put as many number of particles as possible in one particular room. So, then ultimately the problem is very interesting if you have say 5 rooms in this case now look at it here how many partitions I have, I have basically 1, 2, 3 and 4. So, if I have 4 partitions and then I have 3 balls so that problem right now is that how many different ways you are actually permitting these 3 balls and these 4 partitions. Meaning the way I have written it in the in this 3 and 5 way there it could be another possibility. Let me just draw it.

So, suppose I could actually put this thing like this and that two other balls like this. So, ultimately what you are doing is you are permuting these balls and you are also permuting the partitions. So, the number of partitions you see here if they I have actually s degrees of freedom or s rooms you can think about it. So, I have actually s minus 1 partitions. So, ultimately what you are left with is that you can actually have the total number of ways number of ways of having say a v quanta in s oscillators or s number of degrees of freedom or s oscillators because these are all harmonic oscillators is nothing but I will have the entire permutation of them. So, I have total v quanta, and I have s minus 1 partition. So, that will be the answer.

But in doing that you are actually you can also think about it that I have say particle 1, particle 2 and particle 3 like this. But I could actually get another combination that these 2 and 3 gets exchanged. So, that will have one particle in the first room two particles in the second room, but these two particles that arrangement can be also reversed because that way I have drawn it. But these two arrangements are identical because in this case this quantas are indistinguishable.

Now, this is the striking difference for the way we derived the Maxwell Boltzmann distribution and we are doing it right now. For quantum statistics the particles like the Fermions or the bosons whichever you talk about are actually indistinguishable. So, they are identical particles which we did for Maxwell Boltzmann. Here also these are identical particles there is not two different particles statistics, all the particles are same in nature, but in Maxwell Boltzmann distribution those who are distinguishable I can level them as abcd, if you remember the lecture. So, that is how we developed this distribution function which you did not derive properly and we give some hints, and we gave the we derived it in the lecture note. But here the interesting thing is that this now these particles this permutation between the particles you cannot it cannot actually take it as a new distribution because the particles are indistinguishable.

So, I have to divide it by the number of ways the particle scan the quantas can permit among themselves which is v factorial and the number of ways the partitions can also arrange among themselves that will be s minus 1 factorial. So, this is the total number of ways which means this is nothing but our degeneracy or it is related to something like degeneracy. Again why I am calling it as a degeneracy? Because if you remember that I have given some energy and these are the number of possibilities which means actually each of these possibilities given I mean a corresponds to a particular microstate.

So, the total number of microstates which are basically the degeneracy of that level is given by this number. So, now, the question is so how one can get the rate constant from here.

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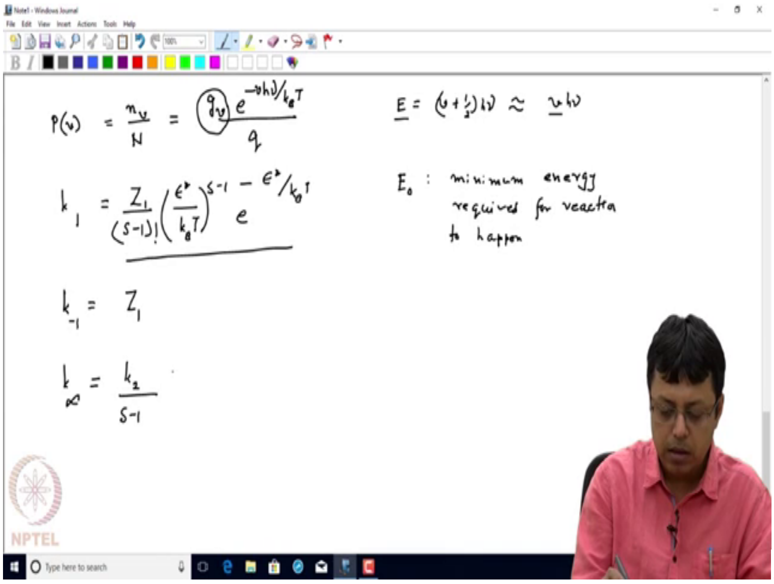

$$P(v) = \frac{n_v}{N} = \frac{\boxed{g_v}\, e^{-vh\nu/k_BT}}{q}$$

$$\underline{E} = (v+\tfrac{1}{2})h\nu \approx \underline{v}h\nu$$

$$\underline{k_1 = \frac{Z_1}{(s-1)!}\left(\frac{\epsilon^*}{k_BT}\right)^{s-1} e^{-\epsilon^*/k_BT}}$$

E_0 : minimum energy required for reactn to happen

$$k_{-1} = Z_1$$

$$k_\infty = \frac{k_2}{s-1}$$

.

So, what we just said is that the probability that the v quantas are in these particular s oscillators, it will be a nothing but something like this degeneration which we just calculated times e to the power minus h nu and by k B T because you know that each if I have actually v quanta the total energy will be v plus half h nu, but that half factor we are right now ignoring. We are just writing it as v into h nu. So, this will be nothing but v into h nu divided by the q and where q is nothing but the partition function which we discuss. So, this is basically the probability distribution. Now, this probability distribution is in quanta you can directly convert it into the energy because you know the relation between E and v. So, if you just multiply by h nu you will give it will give you the probability in energy.

Now, in this way one can actually get an expression for the rate constant and again I am not going into the details. So, what Hinshelwood showed is that for the deactivation process the collisional, deactivation process. You can actually find that in the in the high pressure limit it will be dependent on the Z which is a basically the again we are writing it in terms of the unimolecular rate constant that you remember.

So, this deactivation process you can actually show that will be nothing but I am writing the final expression E 0 by k B t raised to the power s minus 1 into e to the power minus E 0 by k B T, where this E 0 is basically minimum energy that you require for the reaction to happen or we were using actually the epsilon star notation. So, either notation is fine epsilon star by k B T, minimum energy required for a reaction to happen. So, this you will get for the de energization path.

Now, how we get this relationship? Now, basically if you remember there was a collisional activation step, and now we are writing the collisional deactivation step, this will be the collisional activation step not the deactivation. So, it is basically saying, so we made actually two level of theories one the simple primitive thing was k 1 is nothing but the number of collisions Z 1 times the e to the power minus epsilon star by k B T. But that actually takes into account only the external degrees of freedom how many collisions are there and what is the fraction that you are going above this threshold energy which is E star.

And then Hinshelwood said no actually there are also internal degrees of freedom involved and if you attack into account of all these internal degrees of freedom, you can show that this, your g nu I have already showed you like partly how one does it. So, it does all these statistics and then you get this factor. But going from here to here actually you need to apply some tricks, the original derivation and the way you do is that you take them all as a harmonic oscillator and then actually you find the classical density of states so which actually comes from the face list that is why we are not going I mean showing you all the derivation here. And then you can calculate the number of I mean the rate constant for the activation process and again the deactivation process according to any theory is simply the number of collisions I was using the Z 1 notation there.

So, at the infinite pressure the rate constant will be k 2 into k 1 by k, k minus 1. So, it will be nothing but k 2 into s minus 1 and we can write it in a different color.

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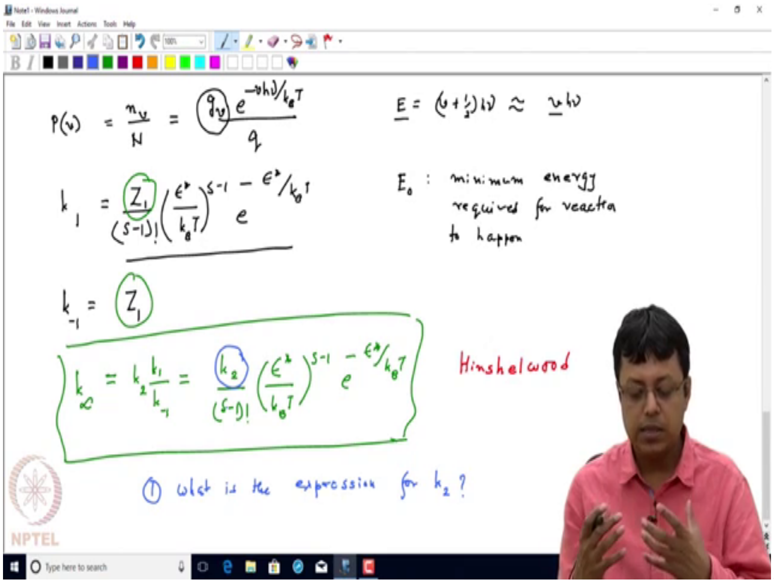

$$P(v) = \frac{n_v}{N} = \frac{q_v\, e^{-vh\nu/k_BT}}{q}$$

$\underline{E} = (v+\frac{1}{2})h\nu \approx \underline{v}h\nu$

$$k_1 = \frac{Z_1}{(s-1)!}\left(\frac{\epsilon^*}{k_BT}\right)^{s-1} e^{-\epsilon^*/k_BT}$$

E_0 : minimum energy required for reaction to happen

$$k_{-1} = Z_1$$

$$\boxed{k_\infty = k_2\frac{k_1}{k_{-1}} = \frac{k_2}{(s-1)!}\left(\frac{\epsilon^*}{k_BT}\right)^{s-1} e^{-\epsilon^*/k_BT}}$$

Hinshelwood

① what is the expression for k_2 ?

So, we say that the k infinity will be according to the Hinshelwood treatment, it will be k 1 by k minus 1 into k 2 which is nothing but now you can see this Z 1 factor will cancel out this factor. And what will be having is nothing but k 2 into divided by s minus 1 factorial into E star divided by k B T raised to the power s minus 1 e to the power minus epsilon star by k B T.

Now, this was a basically Hinshelwood treatment or Hinshelwood equation where he basically showed the unimolecular reaction or the rate of a unimolecular reaction at the very high pressure limit. Now, the question that was remained on that remained unanswered is number 1, like what are I mean like that is the biggest question what is the expression for k 2, because as you can see that k 2 is still remaining. I know the number of degrees of freedom; I can actually estimate the minimum energy requirement k B T is a constant. But then the question is what is k 2?

Now, that problem was tackled first by the other group which in was basically by Oscar Rice and his post up Ramsperger and independently by Kessel and that is why this theory is known as RRK model.

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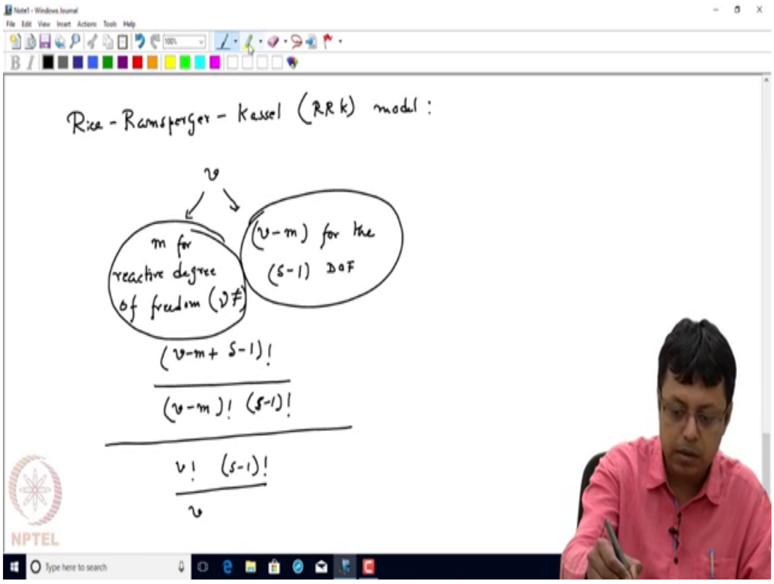
Rice - Ramsperger - Kassel (RRK) model:

$$\frac{\frac{(v-m+s-1)!}{(v-m)!\,(s-1)!}}{\frac{v!\,(s-1)!}{v}}$$

And RRK model basically tells you an interesting way of thinking the problem they said that, ok, fine. So, it does not matter actually, suppose you can actually have an energized molecule, but the reaction will happen when and only when those energized molecules, I mean suppose you put an energy total e or in our language v quanta in that molecule and how this v quanta is partition that we only already have done. But RRK said the reaction probability will be nonzero if and only if out of these v quanta only certain amount of quanta is going into the reaction mode.

Now, what does it mean? That means, actually the way we do it earlier if you remember. So, here as you can see that I have suppose a very weak bond which will dissociate.

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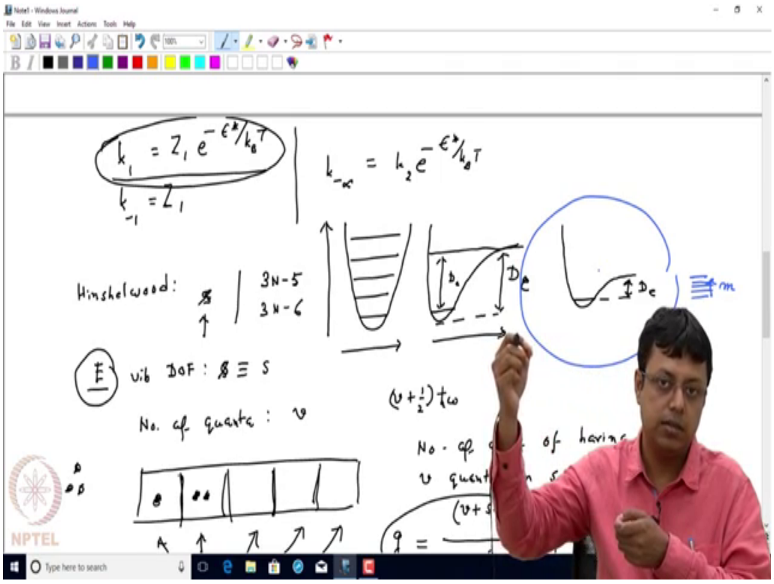

And this energy suppose in the harmonic approximation means suppose I have to supply m quanta because these are all harmonic I mean ladder. And if I do not supply m quanta to this particular mode the reaction will not happen, because the reaction involves the dissociation of the weakest one and that weakest one should get the sufficient amount of quantas. So, that actually it reaches its dissociation threshold and it can have actually more quanta, but it has to have the minimum m quanta.

So, the partitioning right now is a little bit more complicated, it is not like how the v quanta is getting distributed among the s degrees of freedom. It is basically there is one more level of complication and you can show it like this, so I have total v quanta and total s degrees of freedom. So, out of this v quanta what I am saying is that the m quanta is going for one particular degree of freedom which is the reactive degree of freedom and suppose that has frequency which I am calling as nu dagger in I mean like with the similar we are keeping it the similar notation for the biomolecular reaction. And then all this v minus m quanta for the rest of the oscillators and if I have one particular oscillator which I have already considered so all, for all s minus 1 degrees of freedom or s minus 1 modes harmonic modes so that way we have to now partition.

Now, that probability you can also calculate and in this case it is a similar wave. So, I have a basically v minus m quanta and I have to choose one particular like I have, so the way we do it is that I have now this particular thing. So, suppose you remove this m quantum for this you keep it reserved for this particular degree of freedom which is the which has a frequency nu dagger and all this v minus 1 quanta how do you like distribute among s minus 1 degree of freedom.

Now, that requires some like calculation. We can ask this question why I am writing it as s minus 1 why not as s minus 2. So, because I have actually s minus 1 degrees of freedom and considering our partition thing it was it should be s minus 2. But the reason here is that it is basically a joint probability because you have a probability of having this m quanta for this particular mode, and that will also have a probability and that will be multiplied by this probability which you are doing and ultimately when you do all these maths you will get something like that the v minus 1 factorial and s minus 1 factorial.

But this is basically the fraction in which actually this m quanta is going into this reactive mode, otherwise the reaction will not occur and then you have to take the overall probability which means what is the probability independently that these v quanta is going into s oscillator. So, that we have already calculated. So, it is v it will be sorry it is v plus s minus 1 factorial; v plus s minus 1 factorial into v factorial into s minus 1 factorial.

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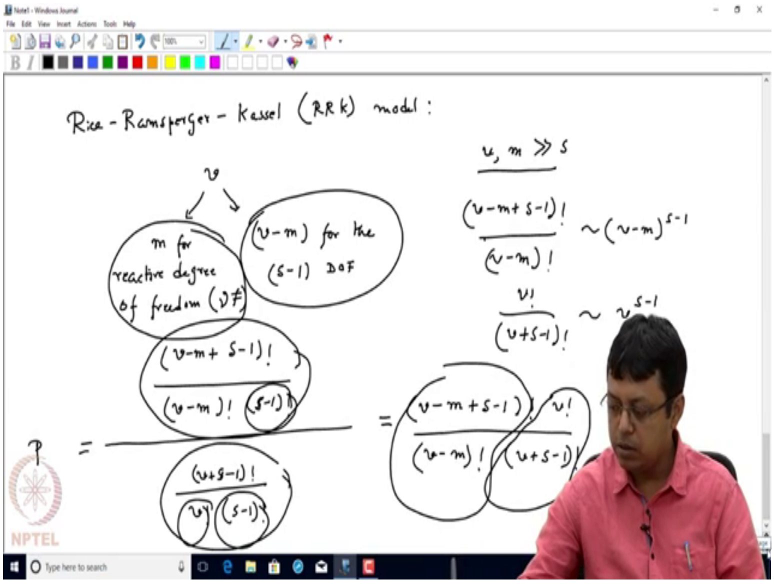

Rice - Ramsperger - Kassel (RRK) model :

$$P = \frac{\dfrac{(v-m+s-1)!}{(v-m)!\,(s-1)!}}{\dfrac{(v+s-1)!}{v!\,(s-1)!}} = \frac{(v-m+s-1)!\;v!}{(v-m)!\;(v+s-1)!}$$

$$\underline{v, m \gg s}$$

$$\frac{(v-m+s-1)!}{(v-m)!} \sim (v-m)^{s-1}$$

$$\frac{v!}{(v+s-1)!} \sim v^{s-1}$$

So, this denominator takes into account of all different ways that you can put this v quanta in s degrees of freedom, but in all of these cases you will not have reaction only in those cases you have reaction, where out of this v quanta only m quanta goes into a particular mode and that is that not that is that number. So, the ratio of the number to the total number of this thing will give you the probability for this particular process. And if you keep on working on this and basically you can make our further approximation like this number will be nothing but you can see here this s minus 1 factorial term that will get cancelled and eventually you will have v minus m plus s minus 1 factorial into v factorial. So, this v factorial is coming in the numerator and then you have v minus m factorial into v plus s minus 1 factorial.

Now, you can further make approximations in the sense that, if I have let us say the v and m. So, you are assuming that your thermal energy k B T is much higher that because that is why the it is its all collisional and it is, so you have accumulated some amount of energy and which is much higher compared to your actual like the, it is basically available some fraction of the thermal energy is available for that and the amount of the quantas like v and this m are much larger than the number of degrees of freedom. Because if the degrees of freedom is very large compared to the available quanta then you can see that the sum of the modes will not still be excited.

So, it is a very less probable that one particular mode will get so many quantas m quantas. If you have enough number of quantas to begin with v and m both are much larger than s then only this will happen, and under that limit you can see that this is v minus m plus s minus 1 factorial. So, that you can now approximate to be something like v minus this factor we can do actually two approximations, but again this is a very I mean under this condition only we are making these approximations that v minus m plus s minus 1 factorial divided by v minus m factorial.

So, this part that actually will go as v minus m raised to the power s minus 1. Now, how we get it? So, you can see here that how I. So, suppose s minus 1 is say 3, so the numerator I will have v minus m plus 3, then v minus m plus 2 times v minus m plus 1 and then it will be v minus m factorial and that will cancel with this denominator. So, I will have basically 3 terms v minus m plus 3, v minus m plus 2 v minus m plus 1, but those again I am approximating each term as v minus m. So, it will be actually v minus n cubed. So, that is how you can approximate this term.

Similarly for this term also you can actually approximate it as v factorial by v plus s minus 1 factorial is nothing but v to the power s minus 1. Now, if I now take the ratios, this probability actually becomes as you can see here. It is now very straight forward it will become v minus m divided by v raised to the power s minus 1 which is nothing but 1 minus m by v raised to the power s minus 1.

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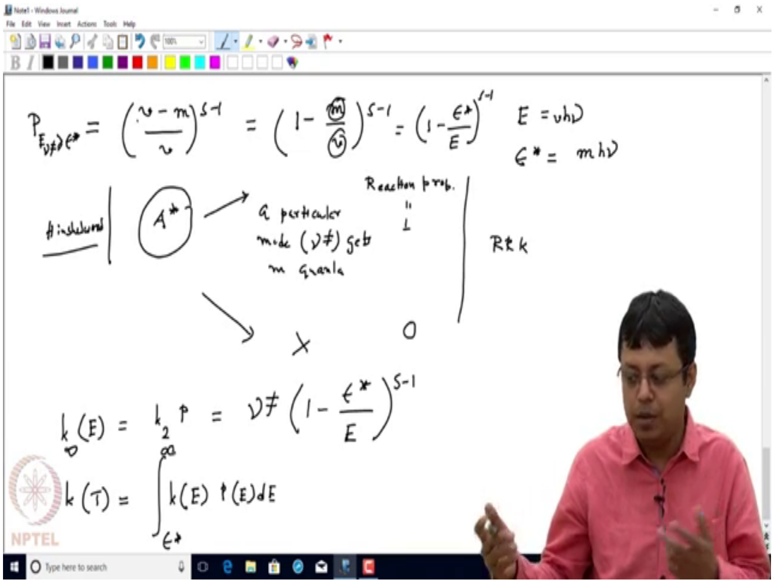

$$P_{E_{\nu\neq}\geq\epsilon^*} = \left(\frac{v-m}{v}\right)^{s-1} = \left(1-\frac{\textcircled{m}}{\textcircled{v}}\right)^{s-1} = \left(1-\frac{\epsilon^*}{E}\right)^{s-1}$$

$E = vh\nu$

$\epsilon^* = mh\nu$

#inshelwood

A^* → a particular mode ($\nu\neq$) gets m quanta

Reaction prob. = 1

↘ × 0

Rtk

$$k_a(E) = k_2 P = \nu\neq\left(1-\frac{\epsilon^*}{E}\right)^{s-1}$$

$$k(T) = \int_{\epsilon^*}^{\infty} k(E)\, P(E)\, dE$$

Now, we can actually write instead of quanta notation you can write that the total energy which is fixed is nothing but v into h nu because we are just ignoring the 0 point energy here and the total energy that we require; so, which we have been writing as E star. Some textbook actually write it as E 0, so we will follow the old notation E star that is nothing but m times h nu. So, then actually we can multiply this numerator and denominator by h nu and convert it into energy it is pretty straightforward. So, then we will get it something like E star by total energy to the power s minus 1.

So, that will be the probability of the basically what is the probability that you get. These, let me just write it very carefully the notation wise. It is actually a probability. Something like in salute calculated, but this probability is slightly different in the sense it says that a particular oscillator which for which the energy the frequency is nu dagger that actually exceeds the A star the threshold energy and for which E star is basically equivalent to the m quantas that probability calculate.

Now, this is basically the probability that the A star molecules, so the difference between the earlier one which is the insolute one is that how the A star is how the internal degrees of freedom is partitioned in the A star. But in RRKM they said that a star will give reaction or the reaction probability if I just write reaction probability will be equal to 1, if and only if I have a certain condition that a particular mode which is the reactive degree of freedom and which has a frequency nu dagger that gets M quantum. And if it does not get then the reaction probability will be 0 something like that and that was the introduction or the of the concept that RRK did over Hinshelwood approximation.

So, and what Hinshelwood did is basically talking about the internal degrees of freedom that was a great advancement thinking in terms of the we were talking about only translational degrees of freedom to the internal degrees of freedom and then you calculate the reaction probability. Now, the question is fine; so those A star will react, but then I have still a problem that ok, fine. So, the ultimately the reaction probability will be k 2 times this probability which we just calculated. It is a function of energy actually, but what is the unimolecular rate then. So, at very high pressure limit which is again dependent on energy because we are talking about only the energy dependent rate constant. Now, that they approximated the RRKM, RRK approximated as this is basically the frequency of that mode itself.

Now, this is something we also did for if you remember we also did for the Irene equation, where we said that I have a transition state and then it is forming reactant and there is a one particular vibrational mode that is giving me the reaction. And then we just have to multiply it by the probability and the probability the way we got it is something like this.

Now, this is the RRK expression for the reaction rate, but usually what you measure in lab is nothing but a temperature dependent rate constant and which you can easily get by taking the energy dependent rate constant, and then calculating this probability which is an energy function of energy. And then you say that I have to make sure that these energies are actually above E star, because otherwise this reaction will not happen because E star is the minimum energy that you need for this reaction to happen.

So, because otherwise if everything is below E star then the m quantas there is no question that there are m quantas there is less than a number of less than m quantas, and there is no chance that this one particular degree of freedom will get m quanta because there is no mm quanta to begin with. So, finally, the if we do all this integration again we cannot show it because it is a beyond the scope of discussion. So, you get the RRK rate expression it is a very simple rate expression you will see that it will be something like a nu dagger into e to the power minus E star by k B T.

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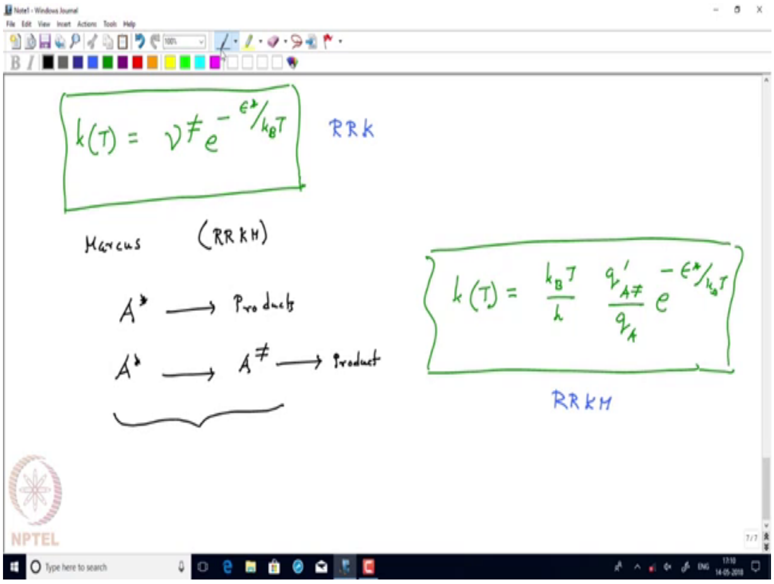

$$\boxed{k(T) = \nu^{\neq} e^{-\epsilon^{*}/k_BT}}$$

RRK

Marcus (RRKM)

$$A^{*} \longrightarrow \text{Products}$$

$$\underbrace{A^{*} \longrightarrow A^{\neq}}\longrightarrow \text{Product}$$

$$\boxed{k(T) = \frac{k_BT}{h}\frac{q'_{A\neq}}{q_A} e^{-\epsilon^{*}/k_BT}}$$

RRKM

Now, what we basically found going from RR sorry this collision theory which is the Lindamann theory to this theory, it is very interesting. And in the collision theory says which is basically the number of collisions remember there was k 2 here and here actually they are saying no actually it is not the k, collision theory itself it is basically the number of vibrations of the vibrational frequency times the energy criteria and that is giving you the RRK rate constant.

Now, the final modification was done by Rudy Marcus, and who modified this RRK theory and that is why this theorem is called RRKM theory. Now, again RRK M theory is beyond the scope of our discussion, but what Marcus did is very interesting. Think I just tell you the salient features what Marcus did and he said that fine in up to RRK you were assuming that I have won a star and I calculate the probability such that so there is a probability such that one particular degree of freedom has an energy which is more than at least equal to or more than this m quanta or E star energy. And that is giving you the reaction that is giving you the products.

But what Marcus did is Marcus assumed that there is some kind of transition state just like a bimolecular transition state that exists before actually a star gives you the product. So, in any sense that RR, going from RRK to RRKM Marcus actually assumed that, ok, so they any unimolecular process first you have a biomolecular coalition and you produce A star. Now, all the A stars will not give you reaction some A stars where actually you have. So, there are actually two criteria first thing first you have to cross the E star energy level, and once you cross the E star energy level second criteria which in salute which RRK said is that fine this E star is ok, but then are you sure that out of this E star m quanta has gone into that vibrational mode. So, that RRK calculated.

Now, those fraction they calculate now the question is how those fraction is giving the reaction then Marcus said that there is an intermediate and it is just like an activated complex there is the intermediate complex again I should not call it as an intermediate. Because it is a transition state and he connected the bimolecular the transition state theory which is developed for biomolecular reaction, bimolecular elementary reaction to the single unit molecular elementary reaction and he did all this calculation based on the density of state.

But finally, at the end of the day surprisingly he calculated this rate constant and the rate constant he found to be equal to the k B T by h and that was, so let me use the original notation that we have been using that is q A dagger with one degree of freedom less divided by q A into e to the power minus E star by k B T. So, that is what RR, is the RRKM rate constant, and now you see the striking similarity with the bimolecular rate constant or the transition state theory which actually says that we have q A into q B because that was bimolecule and this is unimolecular that is what you have only one species q A and otherwise its exactly the same thing.

Now, we cannot show it again because it involves lot of understanding of the classical statistical mechanics which is beyond the scope of discussion, and a lot of understanding of the classical phase space. Because if you remember I told that this transition state theory is inherently a classical theory, because it is basically transition state corresponds to a saddle point in the in the coordinates, in the potential energy surface which is actually has a very precise momentum and position which means it has to be a classical theory inherently. Because if it is a quantum mechanical theory, you cannot describe a point in the first phase, because of the uncertainty principle and because of the commutation relationship more fundamental way.

And then this RRK and RRKM theories are particularly the RRKM theory is also based on very much classical kind of description, where the way we have derived it if you remember that we were writing it as a all these factors as basically summation like I have this n quanta, we are distributing it and we are talking about the permutation and combination. But then if you look at the probability distribution we have been writing it as a continuous integral and there actually they also talked about the density of set which is continuous function of energy not a discrete function. So, there is a difference between the original derivation and the way we showed it, but again we do not derive it fully we just gave you a flavor.

Now, to summarize this part of what we what we said so far we talked about the gas phase reaction dynamics. And we talked about the biomolecular reaction, we talked about the unimolecular reaction, and we showed that for a unimolecular reaction first thing first whether, let us summarize this part.

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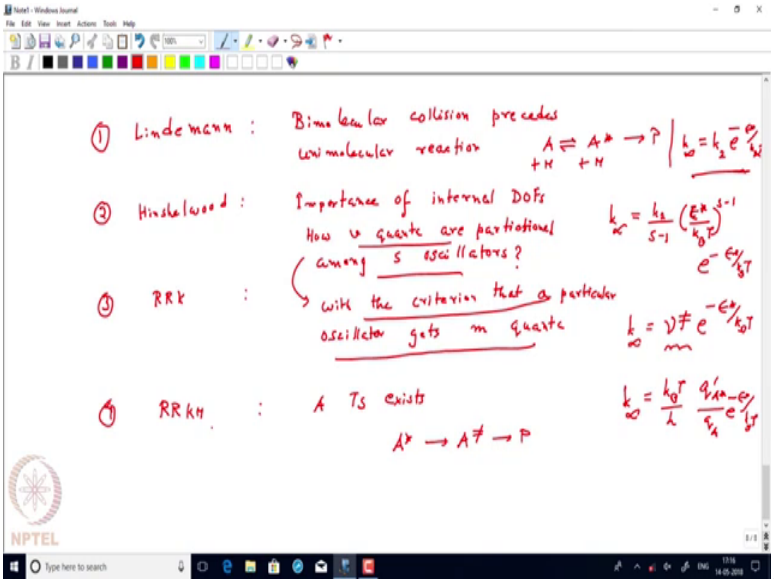

① Lindemann : Bimolecular collision precedes unimolecular reaction $\underset{+M}{A} \rightleftharpoons \underset{+M}{A^*} \rightarrow P$ | $\underline{k_\infty = k_2 e^{-\epsilon_0/k_BT}}$

② Hinshelwood : Importance of internal DOFs $k_\infty = \frac{k_2}{s-1}\left(\frac{E^*}{k_BT}\right)^{s-1} e^{-E^*/k_BT}$

How ν quanta are partitioned among s oscillators?

③ RRK : with the criterion that a particular oscillator gets m quanta $k_\infty = \underline{\nu^{\neq}} e^{-\epsilon^*/k_BT}$

④ RRKM : A TS exists $k_\infty = \frac{k_BT}{h}\frac{q'_{A^*}}{q_A} e^{-\epsilon_0/k_BT}$

$A^* \rightarrow A^{\neq} \rightarrow P$

So, we first said that there is a hypothesis called Lindemann hypothesis. And the Lindemann hypothesis said that a bimolecular reaction, bimolecular collision precedes unimolecular reaction, and this bible molecular collision is the activation process, unimolecular reaction or unimolecular dissociation some textbook write it. And then second and this is basically collisional activation, and he basically said the way that a reacting with M will give you A star and this A star will give you the product.

And then km Hinshelwood and he said that ok, fine. So, from here you can actually get the k infinity to be equal to k 2 times e to the power minus E star by k B T. And then in salute said that for this probability its only the collisional thing, but the internal degrees of freedom also has to be activated otherwise the bond will not break and then in solute found very beautiful. So, he basically said that the importance of internal degrees of freedoms and he said that, so the internal degrees of freedom the internal vibrational modes has to be excited. And he talked about how this partitioning happens and he got a formula like k infinity is nothing but k 2 divided by s minus 1.

We wrote it as we were describing this thing and then I have E star divided by k B T raised to the power s minus 1 into e to the power minus E star by k B T that was the Hinshelwood formulation. And then there was this RRK formulation and who said no actually, fine. So, Hinshelwood found how v quanta are partitioned among s oscillators that is the question he asked. And then RRK said it is similar thing how this thing is happening with the constraint or with the criteria that a particular oscillator a particular oscillator among this s oscillator gets m quanta, otherwise the reaction will not happen and this particular oscillator they said have a frequency nu dagger. And they got a unimolecular reaction rate which is very interesting which is nothing but the frequency of that particular oscillator times e to the power of minus E star by k B T.

Now, in hiding equation you remember that we took it as a nu dagger, but this nu dagger actually eventually cancelled out. So, you do not need to actually explicitly use this formula nu dagger in your calculation. And then 4th thing was RRKM, and he said that a transition state exists between this A star which are giving reaction which has actually not only v quanta in s degrees of freedom, but also m quanta in that particular reactive degree of freedom. And those A stars when they are going undergoing reaction, they actually go over a transition state and that gives you the product, and then Marcus found that this exactly reduces to the hiring like equation for which was developed for bimolecular reaction divided by q A into e to the power minus E star by k B T. So, RRK M theory actually connects the bimolecular reaction dynamics with the unimolecular reaction that means, but these are all developed in the gas phase.

So, we give you a brief introduction on how the reactions happen in solution based on our old understanding on the transport phenomena, particularly the diffusion which will be most important thing to discuss.

Thank you.