Advanced Chemical Thermodynamics and Kinetics
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Lecture – 27
Introduction to bimolecular reaction dynamics 03

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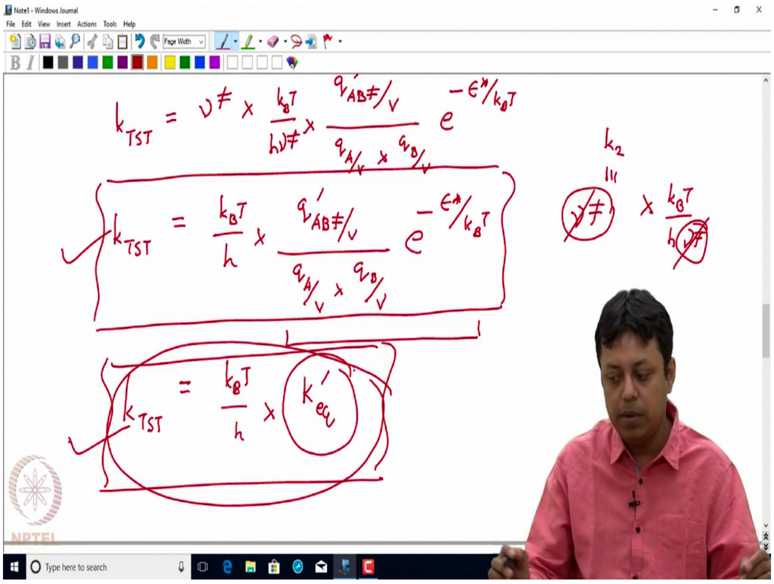

So, now you will use the transition state theory expression to calculate the rate constant for the structureless molecules. And you should get the similar expression which we got in collision theory. Now, one important thing to note here is that we actually said this frequency we which is the characteristic frequency as nu dagger, but we do not need to calculate nu dagger, because we set that k 2 to be identical to nu dagger. And then one factor comes out when we do the calculate the particular partition function the vibrational partition function for the for this transition state and that also gives us a factor which is k B T by h into nu dagger; and this nu dagger now cancels out which you have seen

So, we do not need to actually focus much onto characterize which vibration given rise to the product or we do not need to actually identify the specific reaction coordinate how the reaction is occurring. So, we do not actually need to focus too much on the dynamics. Secondly, as you see here that there is no dynamics here because we did not consider any dynamics here that the molecules are colliding and they are forming on some activated complex, and then it is reacting it is very different from what we the from our approach that we used for bimolecular reactions.

So, for a very complicated molecule like a big polyatomic molecule when they are colliding and they are forming something for a bimolecular elementary reaction, we can write an applied the transition state theory if we know that from electronic structure theory the geometry of the activated complex. And if we can actually calculate the partition functions which are again time independent quantity because these are all equilibrium statistical thermo dynamical properties, and we can calculate the partition functions and then we are done.

So, all we are doing here is basically statistics and the entire dynamics actually is gone and that is the beauty of transition state theory that although you are calculating a rate constant which is a very much dynamical parameter. You are not doing any dynamical calculation explicitly meaning you do not need to explicitly solve any dynamical equation like Newton’s equation of motion or Schrodinger equation of motion. You are just simply doing statistical mechanics and that to time independent statistical mechanics.

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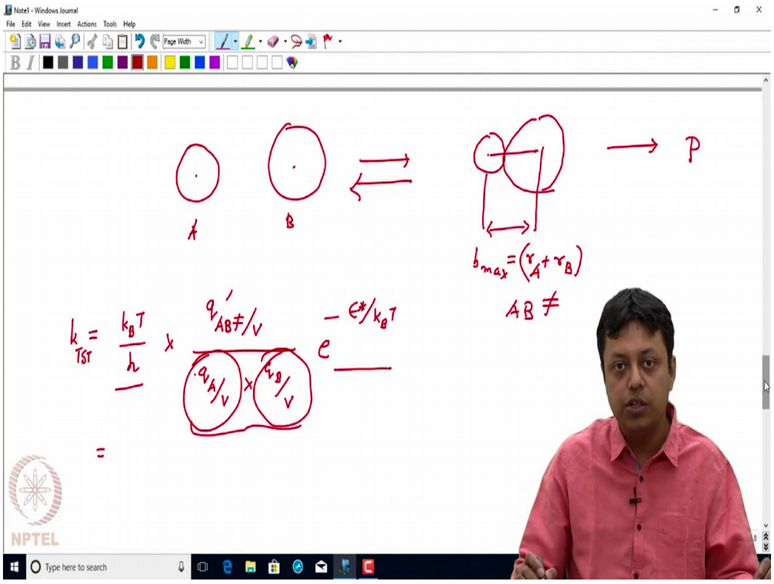

$$k_{TST} = \frac{k_B T}{h} \times \frac{q'_{AB^{\neq}}/V}{(q_A/V) \times (q_B/V)} e^{-\epsilon^{\neq}/k_B T}$$

Now, let us do that. So, for a to say if A and B are something like hard spheres as we said and the transition state will look like something like this, and where this distance which is basically the center to center distance on the nuclear internuclear distance when these two spheres touch each other that we denoted as b max in our derivation for the collision theory which is nothing but the radius of A applies radius of B and this will encounter shown.

So, now let us first try to calculate the partition functions. Now, the expression for the rate constant is for the using the transition state theory is k B T by h, where k B is the Boltzmann constant times we know that we have a partition function for A B dagger per unit volume where we have taken out one vibrational degree of freedom divided by q A by v into q B by v into e to the power minus e star by k B T.

Now, we are going to only calculate this part, and then we can go back to this thing, because this part is similar to the collision theory. And this we will see we will be reduced to a useful version. So, what will be the expression for this thing which is q AB dagger by v with a prime? Now, this is a diatomic molecule. And as you can realize that it has only one vibration right, it is not a diatomic molecule I should say it is basically bimolecular collision, these two are two molecules.

And this is the AB thing, but again it is a crude thing in the sense that the you can think that A and B are touching and then of course, in the transition state there is a vibration for the which is like AB vibration, but this is not exactly the AB vibration. So, this is a oversimplified picture. This is some other vibration that will give me a product because if AB vibrates, it will be again A plus B something like that. But we are talking about a reaction where it gives some product which we do not know.

But we are just trying to mimic the collision theory approach to understand that this gives us the similar result. So, I have AB and here I have AB dagger and now AB dagger in our the way we have drawn it we to for two hard sphere there will be only one vibration and that one vibration already we have let us assume that we have already calculated it. So, in the AB dagger partition function, there will be only translation and rotation and electronic. So, for translation, we know that what is the translation and partition function expression.

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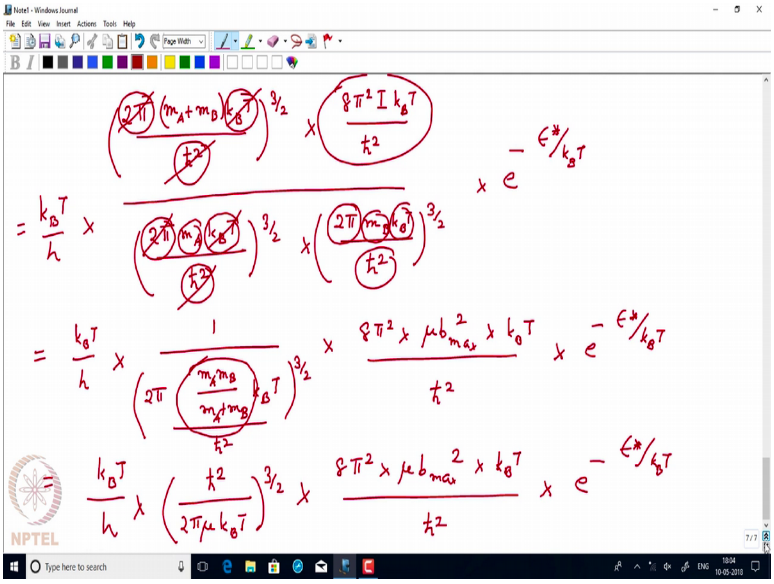

$$= \frac{k_BT}{h} \times \frac{\left(\frac{\cancel{2\pi}(m_A+m_B)\cancel{k_BT}}{\cancel{\hbar^2}}\right)^{3/2} \times \frac{8\pi^2 I k_BT}{\hbar^2}}{\left(\frac{\cancel{2\pi}\, m_A\, \cancel{k_BT}}{\cancel{\hbar^2}}\right)^{3/2} \times \left(\frac{2\pi\, m_B\, k_BT}{\hbar^2}\right)^{3/2}} \times e^{-\epsilon^*/k_BT}$$

$$= \frac{k_BT}{h} \times \frac{1}{\left(\frac{2\pi \frac{m_Am_B}{m_A+m_B} k_BT}{\hbar^2}\right)^{3/2}} \times \frac{8\pi^2 \times \mu b_{max}^2 \times k_BT}{\hbar^2} \times e^{-\epsilon^*/k_BT}$$

$$= \frac{k_BT}{h} \times \left(\frac{\hbar^2}{2\pi\mu k_BT}\right)^{3/2} \times \frac{8\pi^2 \times \mu b_{max}^2 \times k_BT}{\hbar^2} \times e^{-\epsilon^*/k_BT}$$

So, q translation by v we are actually associating the volume with the translational partition function and you know that it is basically 2 pi m k B T by h square raised to 3 by 2. Now, 2 pi m instead of m i have to now take m A plus m B because that is a total mass of the activated complex 2 pi m k B T divided by h bar squared raised to 3 by 2. Then it will have its vibration, vibration we have already taken care of and it will have its own rotation.

And the rotational partition function if you remember the formula it was 8 pi square I, I is the moment of inertia k B T by h per square into sigma. Now, sigma is the symmetry number, but it will be equal to 1, if A and B are different. And let us assume that A and B are different. If it is h, and h then you have to use actually a symmetry number of 2, because one rotation on half rotation gives you the same structure back. So, we are not writing any symmetry factor here. And this is for a linear molecule the rotational partition function. And the way you have drawn it the transition state is also linear because you have a sphere here and then it is basically the rotation of that thing.

So, we are we are assuming it to be a sphere and electronic partition function also let us assuming it to be 1. Let us not write a bother about the electronic partition function right now; let us bother only about the say translational, rotation and vibrational partition function divided by we had q A and q B.

Now, since these are hard sphere, they do not have any other degree of freedom rather other than translational degree of freedom. So, we have to consider only the translational partition function per unit volume for A as well as for B. So, the way we are writing it note carefully, so it is 2 pi m A k B T by h bar square this is for q A by v which you wrote here. And similarly for q B by v, we can also write similar expression 2 pi m B k B T divided by h bar squared raised to the power 3 by 2 times we had k B T by h and times we had e to the power of minus e star by k B T.

So, what we get here, you can notice carefully that I have let us first calculate the 3 by 2 terms. So, I have k B T by h times. So, as you can see I have 2 pi here k B T here and h bar squared here that will cancel with this. So, these things will cancel which is each other.

Now, what I am left with is one 2 pi k B T by h bar squared, so in the denominator. So, what I will have here is 1 over and then also notice that I will have m A times m B and in the numerator I have m A plus m B, so that I can actually write something like m A m B divided by m A plus m B and then I have one 2 pi m A and all the combinations of m A m B and I have also one k B T so and also I have one h bar squared that raised to the power 3 by 2. So, that is the 3 by 2 terms.

Now, you can see that this entire thing is nothing but my reduced mass of the system. So, in the next line what I am going to do is that I will just replace it by the reduced mass mu. Now, before we go there, I also have the rotational partition function as you can see here, so that is 8 pi square and then I. So, what is I? I is moment of inertia now how do you define I, I is basically mu times the r square, but r is basically radius of gyration. And then that is nothing but for this system is b max. So, it is mu b max squared and times I will have k B T and divided by h bar squared times I will have e to the power minus e star by k B T.

Now, we can arrange the terms one by one. And then you see here that I will have k B T, let us also let us write it once again and times I will have h bar squared by 2 pi mu k B T raised to the power 3 by 2. And then I will have 8 pi square into moment of inertia is pi sorry it will be mu b max square not pi, it will be mu into b max squared into k B T divided by h bar squared into e to the power of minus e star by k B T. We have to simplify this expression. So, what I am going to do is that I know that I will just my purpose is to show it as the transition state expression. So, I need one pi b max squared.

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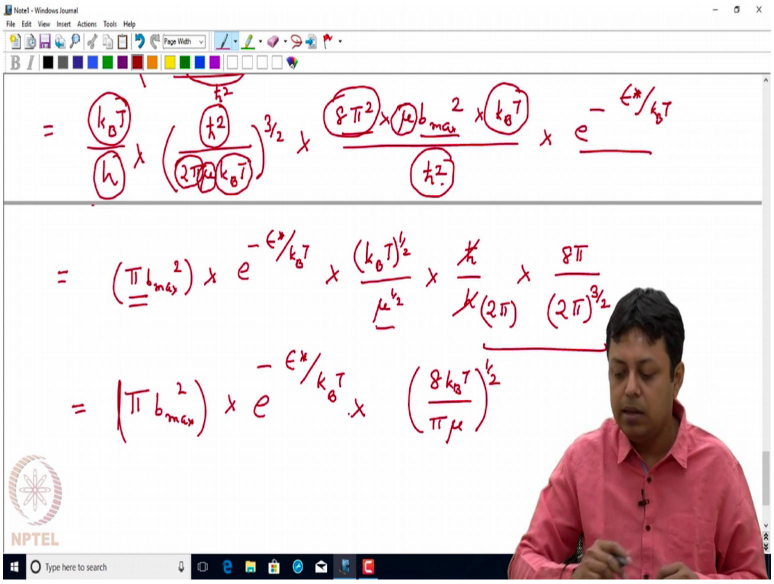

$$= \frac{k_B T}{h} \times \left(\frac{\hbar^2}{2\pi \mu k_B T}\right)^{3/2} \times \frac{8\pi^2 \times \mu b_{max}^2 \times k_B T}{\hbar^2} \times e^{-\epsilon^*/k_B T}$$

$$= (\pi b_{max}^2) \times e^{-\epsilon^*/k_B T} \times \frac{(k_B T)^{1/2}}{\mu^{1/2}} \times \frac{\cancel{\hbar}}{\cancel{h}(2\pi)} \times \frac{8\pi}{(2\pi)^{3/2}}$$

$$= (\pi b_{max}^2) \times e^{-\epsilon^*/k_B T} \times \left(\frac{8 k_B T}{\pi \mu}\right)^{1/2}$$

So, I can still one pi from here and the b max squared also I am just skipping. So, I am just writing it as pi b max squared times I am also keeping this thing untouched e to the power minus e star by k B T and then let us see what we are left with. So, we are left with one k B T by h here. Let us first calculate the k B Ts. So, what we have k B T here and then I have one k B T here. So, these two gives me k B T squared and then in the denominator I have k B T to the power 3 by 2. So, it is k B T squared divided by k B T to the power 3 by 2 k B T square is k B T to the power 4 by 2. So, together I will have k B T to the power of half. And then what else I have one mu here and I have mu to the power 3 by 2 in the denominator. So, I will have mu to the power half in the denominator.

And now let us calculate the h, so I will have h here and I have h bar squared here. So, let us calculate the h bar first. So, h bar squared and h bar squared here they will; so it will be h bar squared and h bar squared. So, I will have h bar to the power half, but then also h bar is nothing but h pi 2 pi. So, in that sense, I can write it as h by 2 pi and then we can easily figure that out how it gets cancelled. So, let us just do it. So, this h is I have one h here as you can see, and then I will have one h bar squared here. And I will have h bar to the power 3 by 2 h bar square to the power 3 by 2, so which is h bar cubed and then I will have one h bar squared instead of h bar.

So, let us write it once again. So, I have this h bar squared and h bar cube, so I have h bar divided by h and that will give me basically 1 over 2 pi eventually times what I have let us also calculate the 2 pi's I have 2 pi here. And I have 8 pi here because already one pi we took out for pi b max squared. So, I have 8 pi divided by 2 pi to the power 3 by 2 8 pi divided by 2 pi to the power 3 by 2 something like that, so that also can simplify. So, this is 2 pi and 2 pi to the power 3 by 2, it will be 2 pi to the power of 5 by 2 and then this is a pi here. So, this is simplify that thing.

And ultimately what we will get is these 2 and 2 to the power 3 by 2, you will get the value of 8 k B T by pi I have a mu here also the entire thing raised to the power half. And then I have basically already derived the transition state see sorry the collision theory expression. And we see that the expressions are exactly the same all right. Now, let us go back and look at the other expression for this collision theory, where we showed that not collision theory transition state theory, where we showed that this entire thing the expression can be written as k B T by h into some equilibrium constant.

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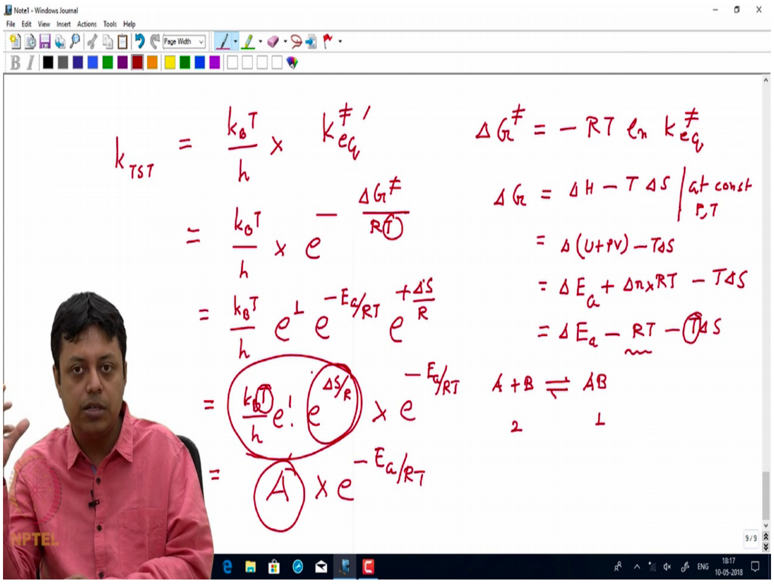

$$k_{TST} = \frac{k_BT}{h} \times K_{eq}^{\neq\,\prime}$$

$$= \frac{k_BT}{h} \times e^{-\frac{\Delta G^{\neq}}{R\boxed{T}}}$$

$$= \frac{k_BT}{h}\, e^{1}\, e^{-E_a/RT}\, e^{+\frac{\Delta S}{R}}$$

$$= \frac{k_B\boxed{T}}{h} e^{1}\, e^{\Delta S/R} \times e^{-E_a/RT}$$

$$= \boxed{A} \times e^{-E_a/RT}$$

$$\Delta G^{\neq} = -RT \ln K_{eq}^{\neq}$$

$$\Delta G = \Delta H - T\Delta S \Big|_{\text{at const } P,T}$$

$$= \Delta(U+PV) - T\Delta S$$

$$= \Delta E_a + \Delta n \times RT - T\Delta S$$

$$= \Delta E_a - RT - \boxed{T}\Delta S$$

$$\underset{2}{A+B} \rightleftharpoons \underset{1}{AB}$$

Now we can rewrite it as k TST is nothing but k B T by h into I have some equilibrium constant for reactant to transition state equilibrium, but with the prime and the prime denotes that the one degree of freedom is less. Now, what we can do is that we can apply just classical thermodynamics. And we know that the relation for the equilibrium constant with the change in the free energy. And we are going to just use that relation. So, we already know that del G is equal to minus R T l n k equilibrium. In this case it is for the transition steps, so I am writing it as a del g dagger. So, this is k equilibrium dagger with a prime sign or we can just keep the prime sign whichever it is. It denotes basically equilibrium between the reactant and the transition states.

Now, what is a, if we just write it, so you can easily get the expression as e to the power minus del G dagger by R T. And remembering that del G dagger has one degree of freedom this. Now, what is del G? Del G is at constant pressure and temperature it is del H minus T delta S, of course, it is at constant pressure and temperature that is why we got this expression. Now, what is del H? Del H is nothing but del of U plus P V, if it is an ideal gas assuming an ideal gas behavior and it assuming a gas phase reaction.

Now, we have actually delta U, delta U is the change in internal energy that is connected to the activation energy which Arrhenius has got experimental because this is a macroscopic quantity which we measured. And e star or epsilon e star that notation is a microscopic quantity which actually denotes from the zero point energy differences. And delta P V, now P V actually you can approximate a further as ideal gas equation. So, in the previous case when we write it a H is U plus P V that is not for ideal gas solution that is by definition of enthalpy.

And now we are applying the ideal gas equation, and where actually it is a delta of n R T. Now, R T is a constant. So, it is nothing but delta n times R T minus T into delta. So, delta n here is basically the change in number of moles. Now, for our reaction if you think that I had a bimolecular reaction and that is forming a transition state which is just one molecule. So, the change in number of moles is basically minus 1, because I had two moles here and one more here. So, it is 1, minus 2, it is minus 2.

So, you can write out a write that it is nothing but delta E a it will be a minus sign here, so minus R T minus T delta S. I can put it back into this equation. So, what I see here, it is k B T by h times e to the power minus. So, first I am writing this term R T term. So, e to the power minus R T by R T minus R T by R T, it will be basically just or e to the power plus 1 times I will have a factor which is e to the power minus E a by R T. And then I will have a factor which is e to the power minus not minus it is a plus sign delta S by R, because there was a T here, it cancels with this T here.

So, we can just rearrange the stuff which is k B T by h into e to the power minus E a by R T or we can actually keep all these form like k B T by h into e times e to the power delta S by R times e to the power of minus E a by R T. Now, you see that this has a similarity with the Arrhenius equation. Now, the question is what we get from this derivation is an expression for this A, which is the pre exponential factor. Now, what is the physical significance of the pre exponential factor which we just derived from transition state theory?

Now, what you see here is a very interesting thing it has a k B T by h factor and then there is a e, e is a constant and it is a temperature dependent of course, because there is a T here. Now, it has this striking factor e to the power delta S by R. Now, that is an entropic factor. Now, think about it if we have a two body like A and B bimolecular reaction and then is forming the transition state. Then the transition state is a just one molecule you can think of it. So, in some sense actually transition state is more ordered because as you see that the change in entropy in this case is negative, which means the overall reaction probability will decrease once you go from the reactants to the transition state.

If that actually makes sense because when you do make a derivation from the collision theory, you actually calculate all these the a actually that is related to the number of collisions. Because you if you remember this collision cross section pi b max square times the relative velocity and these two thing gives you basically the number of collisions terms. And then there is an energy factor which is e to the power of minus e, but some energy by R T. But then you say that that energy factor takes care of the fact that all collisions does not give you the products only those collisions which can cross a certain amount of energy will give you the product. But then we always overestimate the reaction rate.

The meaning of the overestimation is this that you your transition state has to be nicely oriented. In a sense like we always said that this A and B are kind of structure less in this case, but in reality A is the molecule, B is a molecule and they have to actually collide in the right fashion. For example, suppose if you are talking about collision between two molecules, but these molecules had two functional groups which are like this, then these two functional groups would interact with each other like this. So, if the collision happens like this, although the energetically the collision may be favorable orientationally it may not be favored.

So, this orientation factor is directly embedded in the entropic factor. So, you have to have the right arrangement which will reduce the entropy of the system, because you are going from a less organized structure where the reactants are randomly moving around to a more organized structure in the transition state for which the entropy should decrease. And then actually you can have a decrease in the reaction probability which you calculate, which actually takes care of the all the orientational factor that you did not account for when you did collision theory expression. This is how we can actually understand how the transition state theory can give me an interpretation of the pre exponential factor, in terms of the probability factor which directly relates to an entropic factor.

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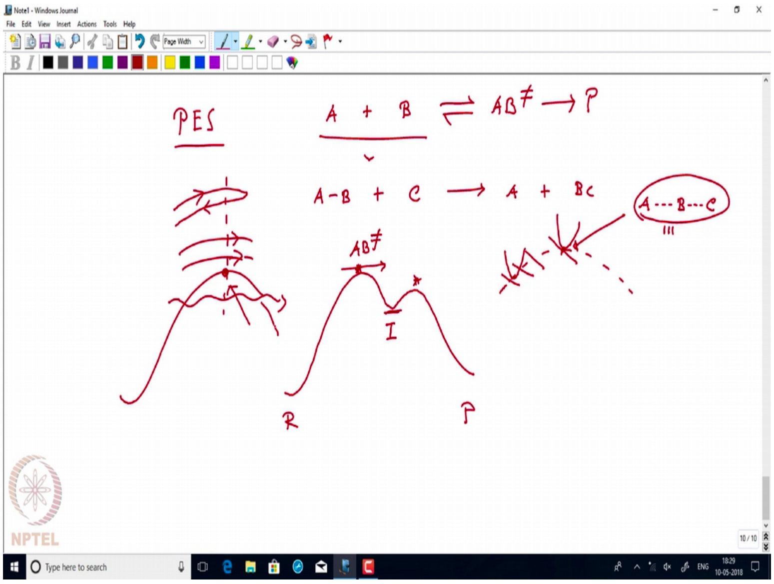

Now, let us summarize this part. So, what we did in this part is that we first started with a discussion on the potential energy surface. Now, for a potential energy surface, we talked about always by molecular reaction. And then we for developing the concept of the saddle point, we said we considered a reaction where actually a atom reacts with a diatom. It is also kind of a bimolecular reaction where one molecule is a diatom; and the other molecule is just a monatomic molecules something like that.

And then we talked about a reaction like A plus B C, and we draw the potential energy surfaces. And we found that the reaction actually goes through a minimum energy path, minimum in the sense that whenever it moves it actually moves along a minimum path which is minimum in the orthogonal direction, but then it actually goes to a maximum and when it reaches it maxima it means that it is since it is always at the minima position in all other orthogonal direction, this point represents maxima in one direction and minima in all other direction.

So, it looks like a saddle and that saddle point you can think that the geometry of the saddle point is something like neither the AB bond is broken not the BC bond this completely form. And you call this thing as a transition state geometry. And this entire thing you call it as a complex and you call it as activated complex. Now, then you formulate your theory, and you say that this activated complex is in equilibrium with the reactants. So, you can actually directly go from here.

So, A plus B is in directly in equilibrium with some activated complex and that gives rise to the products. And then you say that fine if it is in equilibrium I can directly use the equilibrium approximation. And then you say that the rate of product formation that we directly connected to the vibration of the activated complex. And the rest of the thing can be equated to an equilibrium constant which can be connected to the partition functions.

And then you cleverly calculate the partition function, where you separate one degree of freedom from the rest of the degrees of freedom, and that one degree of freedom which shows as a vibrational degree of freedom. You could also solve it as a translational degree of freedom in that sense actually you say that the entire molecule or the inter activated complex as it is moving across the transition state.

And that translational degree of freedom you take into account, and you will get the similar answer you will get the same (Refer Time: 27:31) equation k B T by h with the multiplied by all this thing. But they are actually do one degree of less in the translational degree of freedom we can actually give you problem set where you will be asked to derive it in a step by step. And then what you see here is that you can get an AB dagger and this AB dagger of the statistical properties of this AB dagger will control everything,

everything in the sense if you can know the geometry of the molecule, you can actually calculate the partition functions. And then you can calculate the rate constant and that is the entire essence of the transition state theory.

And then we give an example for structure less molecules like a hard sphere molecules collision and ensure that it right. Away reduces to the expression for the bimolecular collision theory. And then we said that for any transition state for a very complicated system, there you can think that there is a specific orientation for the transition state. So, there is a geometry factor involved and that geometry factor pushes the requirement that it is connected to an entropic factor. So, the entropy actually is decreased because you are going from more random set to a more ordered state. And that accounts for the why actually you overestimate the reaction rate constant when you do it in a collision theory experiment a collision theory way.

So, you can actually meet the correct energy requirement, but you may not be able to meet the correct orientation factor because there is no way you can actually think about the orientation form a hard sphere model. Because these are structure less. But you can incorporate into the transition state theory, and you can physically interpret it as an entropic factor.

So, in the in the next set of lectures, we will see that how one can actually think about so this is a basically a transition state theory developed for by molecular reaction, but similarly we could actually develop it for unimolecular reaction. But again for unimolecular reaction, we discussed the Lindemann hypothesis which talks about a bimolecular collision that precedes a unimolecular reaction. And then this energized molecule in the unimolecular reaction and gives rise to the product.

But we will see if we can apply the similar transition state concept or the statistical concepts to understand to get a derivation for expression for the rate constant. Also as a final note as we discussed that the transition state exists at a saddle point, it is not always true because there are many sophisticated version of this transition state theory which basically talks about the trajectories for going from reactant to product. And then there in the detailed quantum dynamical conclusion shows that there could be some trajectories which actually come back on the near the transition state region.

So, you may if you calculate at the number of trajectories at the saddle point, you may not get the correct answer because actually you might have a recrossing a near the saddle point. So, they are actually you talk about a position of the transition state to be the position where the number of recrossings are minimum. So, this is called a variational transition state theorem. And I am not going into the details into that.

Secondly, this transition state theory when you can we derived it as a motion on the potential energy surface and this is just one version of the transition state theory. There are also many other versions and this version as I said that it is known as activated complex theory, because we talked about a complex. But these complex if you remember that this is not a stable complex, because you have a barrier along the reaction coordinate. A complex means which is stable in all degrees of freedom along all degrees of freedom meaning reaction intermediate will be something like which has a minima even along the reaction coordinate. And so these are basically the transition state going from say a reactant to a bunch of reactant to a bunch of products and this is an intermediate.

So, in some sense we although we used the same concept that I have a reactant and d t which is in equilibrium with the intermediate, and we use the same pre equilibrium constant pre equilibrium concept for trani for development of transition state theory. But there you have to be very careful this is actually a transition state this is not exactly an intermediate and which is aligned at the minima and all other direction, but at a maxima along the reaction coordinate.

So, it is not really a complex, so that is why this activated complex theory and this named complex is little bit misnomer. And thirdly which is most important this location of the transition state the way we derived it is right at the saddle point or you can think of it is at a particular point where actually there recrossings are of the trajectories are minimum, but the point here is that it has a very precise location.

Now, you could actually cast the entire problem instead of the say coordinate space energy versus coordinate space to a face spaced problem where you represent the momentum and a position. And there also you represent the transition state as a form. If you have a point in the first phase which means actually you are simultaneously specifying the momentum and the position with absolute precision which means you are violating the uncertainty principle, which means actually transition state theory is inherently a classical theory. And this point was made by Wigner and who did all this classical canonical partition function derivation which also we did not derive. We just derived the adding model which is not very rigorous model, but it is a correct model in the sense that ultimately at the end of the day the Wigner’s model with all this reversed derivation also gives you the similar expression.

And the transition state theory had many drawbacks. And many more discussion as we just said that the variational transition state theorem. There are also tunneling effects in the sense that when you go from reactant to products, you may actually tunnel through the barrier and at low temperature this tunneling can contribute significantly to the reaction rate constant, but those details we are not going to discuss in this course. So, we will just stop our discussion on potential energy surface and transition state theory here.

Thank you.