Advanced Chemical Thermodynamics and Kinetics
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Lecture – 28
Introduction to bimolecular reaction dynamics 04

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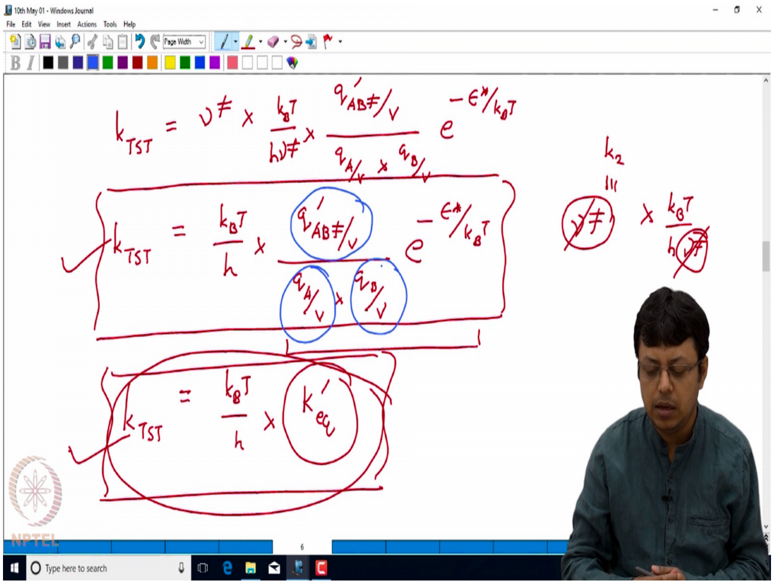

$$k_{TST} = \nu^{\neq} \times \frac{k_B T}{h\nu^{\neq}} \times \frac{q'_{AB^{\neq}}/V}{q_A/V \times q_B/V}\, e^{-\epsilon^*/k_B T}$$

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

$$k_2 \equiv \cancel{\nu^{\neq}} \times \frac{k_B T}{h \cancel{\nu^{\neq}}}$$

$$k_{TST} = \frac{k_B T}{h} \times K'_{eq}$$

Now, let us see an interesting application of the transition state theory rate expression that we already derived. So, we have to calculate the partition functions to derive any expression for a particular say bimolecular reaction. So, in order to see that this expression is actually equivalent to our Collision theory expression, let us proceed.

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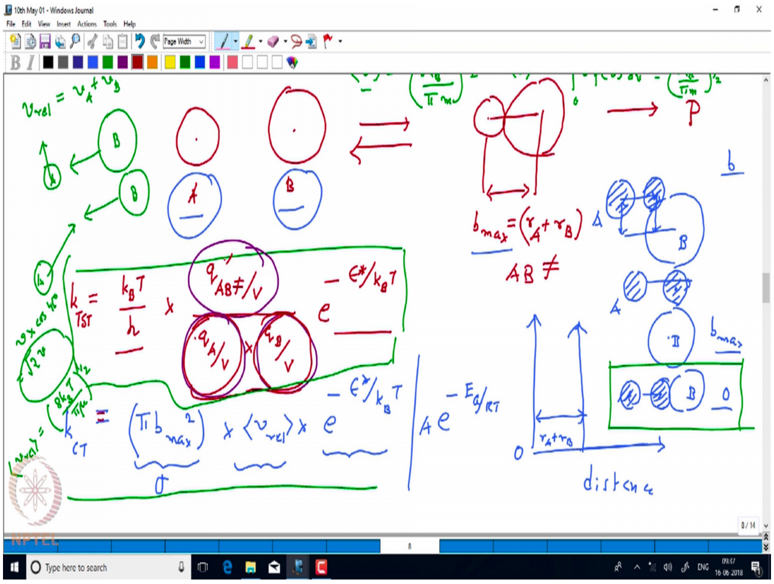

And here what I have drawn is basically just to give you a feeling, what we are talking about. So, remember that in we had suppose a bimolecular reaction and between 2 atoms or molecules and these atoms and molecules, we are approximating A and B denoted the atoms are the molecules. And, then we are approximating these shape of these atoms or molecules to be spherical and these are hard spheres in the sense that the if I plot the potential energy between them as a function of the distance between them. So, as soon as so, the potential energy will be 0, but as soon as these 2 atoms or 2 molecules touch the potential energy goes to infinity. And that happens when that center to center distance is basically the addition of the radius r A plus r B which we call as b max.

So, b is usually in this scattering theory is defined as an quantity called impact parameter and so, it is defined as suppose I have 1 atom or molecule which is a sphere and then the other 1 is approaching at a angle something like this. And then you will see that center to center distance actually varies, in the sense that we could have many different possibilities like this can go like this and suppose the atom A is in stationary position I we are actually denoting the atom B as the, the bigger 1 has atom B.

So, let us stick to that convention and this is A. Now if A comes like this then we can actually have after some time is just touching the B. So, that is the maximum position of the impact parameter in the sense the center to center distance is just as addition of r A plus r B. However, we can have another possibility that A is coming like this and then when they collide as you can see from this picture the center to center distance is now less than the b max or less than the some over radius of the 2 atom. And you can also have a head on collision like A is coming towards the B and then as it approaches then it just has an head on collision and that time the center to center vertical distance is basically 0.

So, this B can be many I mean can take values between 0 and b max and this b max is very important in Collision theory because we know that the if the atom A or the molecule A lies within, distance b max from the center of the other molecule or atom then the collision will happen which is very clear from this picture. Now, in Collision theory we use this b max and then we get a rate expression something like if we write it as k C T is basically a collisional cross section which is pi b max square. So, which sometimes we write it as a sigma collisional cross section times the average of relative velocities.

Now, what is the average of relative velocity I will come to that and time some energy which is basically equivalent to the minimum energy requirement in Arrhenius. It is not exactly the same energy as we see in Arrhenius expression remember the Arrhenius expression was k is basically A into e to the power minus E a by R T. Now, that E a is slightly different that because that is actually a measurement measured E a.

So, it is basically the energy Arrhenius found through experiments that the minimum energy that is required and interpreted it as the minimum energy, but although it is basically when we do the experiment it is done on a statistical ensemble of atoms or molecules which are undergoing the reaction. So, this E a capital E a is kind of an average energy. Now, what we are talking about right now E star is basically from a very quantum mechanical point of view, but we have a potential energy surface something like we draw earlier.

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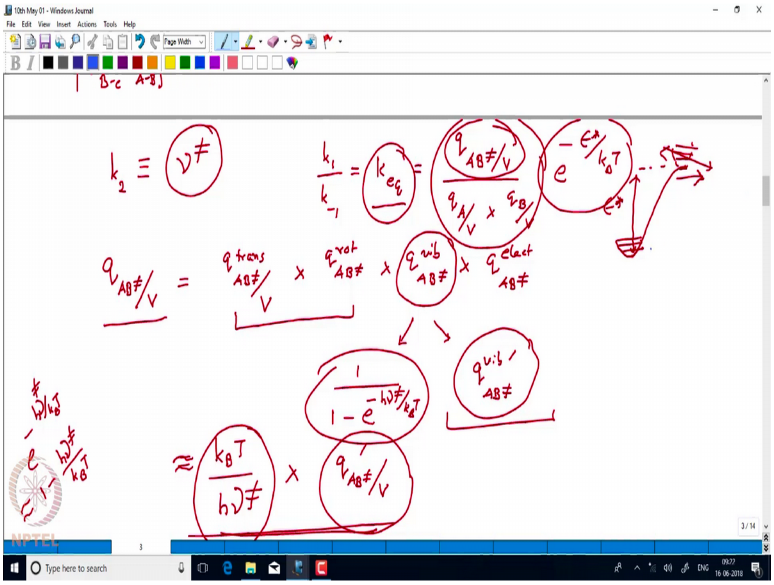

$$k_2 \equiv \boxed{\nu^{\neq}}$$

$$\frac{k_1}{k_{-1}} = \boxed{K_{eq}} = \frac{q_{AB^{\neq}}/V}{q_A/V \times q_B/V}\, e^{-\epsilon^*/k_BT}$$

$$q_{AB^{\neq}}/V = \underbrace{q^{trans}_{AB^{\neq}}/V \times q^{rot}_{AB^{\neq}}} \times \boxed{q^{vib}_{AB^{\neq}}} \times q^{elect}_{AB^{\neq}}$$

$$\frac{1}{1-e^{-h\nu^{\neq}/k_BT}} \qquad q^{vib'}_{AB^{\neq}}$$

$$\approx \frac{k_BT}{h\nu^{\neq}} \times q'_{AB^{\neq}}/V$$

$$e^{-h\nu^{\neq}/k_BT} \quad 1 - \frac{h\nu^{\neq}}{k_BT}$$

So, here E a has a meaning of E star has a meaning of like this. So, it is basically the energy difference between the 0 point energy and the 0 point energy of the transition state something like that we have in mind. And then what we are saying is that expression will basically, the e s e star of the minimum energy expression will go as a Boltzmann factor which we derived in the earlier course in thermodynamics and kinetics which you can also see in your, recommender texts.

And then you have a another term which is the relative of the average of the relative velocities. Now, what is average of relative velocities now as we just said that the approach of A towards B, if we think that B is stationary because everything is in the relative frame it can be many ways. So, in this picture where we showed that these 2 are having a head on collision in that case the angle of approach is basically 180 degree because as you know that A is B is moving in this way, A is moving in this way. So, the relative velocity will be added up. So, in that case the v relative will be v A plus v B. Similarly the relative velocities can be also at 90 degrees like atom B can move like this atom A can move like this.

So, the approach is there 90 degree and then you can have also in between situation like atom B is moving in this direction, but A is moving like this which means actually if I think about all these angles like from 0 degree to a maximum of say 180-degree and so anyway. So, we have to think about the relative orientation of the relative factor. As you can see that at a 90 degree there will be no collision because the vector added by a vector addition, we will see that these vectors are also along. So, what we can argue from here is that if we want to calculate the relative velocity that then we have to think that as if these 2 things are colliding, but at 45 degree to each other and then we have to take the relative velocity component.

So, which means actually you have to take the if I have say a head on collision like we add up, but this adding up comes basically from cosine of 0 degree, because we have a 0 degree collision here, but if we have a 45 degree collision then and if the atoms are of same type. So, then I have to take just the relative velocity as not v plus v which is 2 v if the atoms or the molecules are same, but I have to take v into cos theta where cos theta is 45 degree. So, I will have basically root 2 into v.

Now, you know that the there is a relative average velocity expression. If the average velocity expression is basically comes from Maxwell Boltzmann distribution of molecular speed, I should not call it as a velocity it is basically average speed. Now that expression has formed something like this, it is 8 k B T by pi m raised to the half. So, it is basically comes from you can easily calculate how to find out this average velocity, you have to just take the velocity. And, since you are calculating an average you have to take multiply if the probability distribution which is the 3 dimensional Maxell Boltzmann distribution for molecular speed and then you have to integrate over all the possible speed and that will give you this value 8 k B T by pi m.

Now, if I have actually this kind of situation square root of 2 v and it can be easily shown that for our relative velocity, we can write a similar expression, but it will be nothing, but 8 k B T by pi mu where mu is basically the reduced mass of the system right mu is nothing, but m a plus m A m B by m A plus m V. So, we can easily, formulate that, it is very easy to show. Now coming back so, this is basically Collision theory net expression. Now, if for this is true for any 2 structure less atoms or molecules or the collision between them which is a by molecule collision the same expression we should also get from the transition state theory, but for the time being as you can see that the expression which we have got from colleague transition state theory is rather much complicated.

And it actually involves the partition functions, but we can show that for atom die atom or any collision like this we can actually show that for structure less systems who are actually, you can think that initially the atoms of the molecules which are participating in the reaction has only translational degree of freedom. Then the 2 theories are very much equivalent and remember that you may think that it is not equivalent for a complicated molecule which is large enough and where actually we have lot of initial vibrations and initial rotations, but you have to also remember that the collision theory model which we just discussed is also a very simple model because that is also dependent on the hard sphere.

So, this model applies to hard sphere and we got an expression. So, the logic is that for hard sphere that kind of model, the transition state theory also should give us a similar expression. Now, there are also modified version of collision theory or which is known, in generally known as the Scattering theory, but those we are not going to discuss and they are actually you can calculate the scattering cross section from either classical mechanics or actually talk about a scattering potential. And, then talk about a deflection angle from the different capital of the scattering cross section and they depend incorporate the quantum effects very intelligently to it. We again modify the expression for the cross section and then you can actually calculate the rate constant, but we are not going into the details and those are detailed calculation now show exact similarity with or near exact similarity with the transition state theory even for polyatomic molecules.

Now, coming back to our discussion we have to calculate the partition functions and remember the, I will just write the partition functions once again just to remind you. So, you can actually go back and have your note where we discuss the statistical thermodynamics and we calculated the molecular partition functions for different degrees of freedom translation rotation and vibration. So, and electronic partition function we said that we always take it to be 1.

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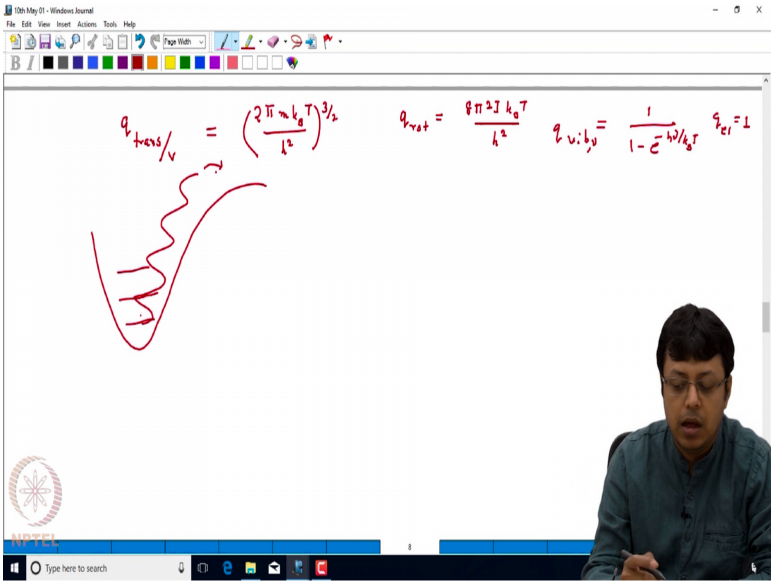

$q_{trans}/V = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$

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

$q_{vib,v} = \frac{1}{1 - e^{-h\nu/k_B T}}$

$q_{el} = 1$

So, instead of Z notation I will be using old notation which is the q notation. So, we know that q translation and usually the translational partition function is expressed per volume and that is why if you see here that for both the transition state as well as the reactants we have written part volume, partition function for volume, but this volume part gets associated with the translational volume part.

So, q translation is nothing divided by volume, if you remember that it will be 2 pi m k B T divided by h bar square and if it is a 3 dimensional problem, we will have 3 by 2. And there is an L in the translational partition function expression and that L cube gets transferred into V and that is what we have done basically we have divided the transition partition function divided by V. And then so, this is translational partition function part will follow and then similarly we can have the rotational partition function and that is 8 pi square I k B T divided by h square into sigma.

Now, sigma is basically the symmetry number in this case if we assume that A and B are different then we do not need to actually consider any sigma for here, but for homonuclear diatomic molecule for example, we have to choose sigma to be equal to 1, the reason is a part half rotation, it basically creates exactly the same structure and you can easily visualize it like if I have an h 2 molecule. For example, so, if I just rotate it by 180 degree. So, not by 360 degree, you will see a similar structure and that actually has a much deeper consequence in terms of the symmetry of the molecule and how it is connected to the energy levels of the molecule.

And we can actually figure out that there are basically the rotational quantum states are can be split into 2 ways which are basically the odd J states and the even J states and one corresponds to the something known as off hydrogen and other corresponds to the para hydrogen and it depends on the nuclear spin formulation. So, we are not going into the details you can actually get all these details or in your actings physical chemistry textbook which is 1 of the textbook recommended to you and there is a chapter on the statistical thermodynamics. And you can actually look up there and you will get a fairly good explanation of this symmetry principle how it is applied to the spectroscopic lines or the number of degeneracies for the rotational transition.

Now, for our case actually; so, as we said that symmetry number is not necessary just take it to be 1 and similarly we also have q vibration which we already know that q vibration for any particular vibrational mode will be 1 divided by 1 minus e to the power minus h nu by K B T, but that is for the nu th moment. So, it should actually write it as a subscript as nu. And then the electronic partition function, we are usually using it to be taking it to me 1, thinking that it is all the reactions are happening in the ground electronic state because if you remember the potential energy surface that the reactants are basically promoted.

So, there are vibrational levels. So, there the reactants do some translation and vibration and there now promote it to an energy level. So, that actually they can acquire a configuration of a transition state and such that they can now react. So, that promotion gives the active, necessary activation energy and necessary geometry also and when they are promoted that reaction will basically occur, but everything is happening in the ground state for energy surface, it is not like that we are basically doing a photo chemistry whoever actually we are going to the excited state and doing the reaction.

In that case partition function may change because the reaction is happening and different electronic surface which can be for example, a triplet state and in that case I have to take it to be q to electronic which 3. So, in general for without if you do not have too many complications of the atoms of the molecules which are reactants we can actually take the electronic partition function to be equal to 1 because most of the molecules also of the ground electronic states all the electrons are there and it is a singular sate.

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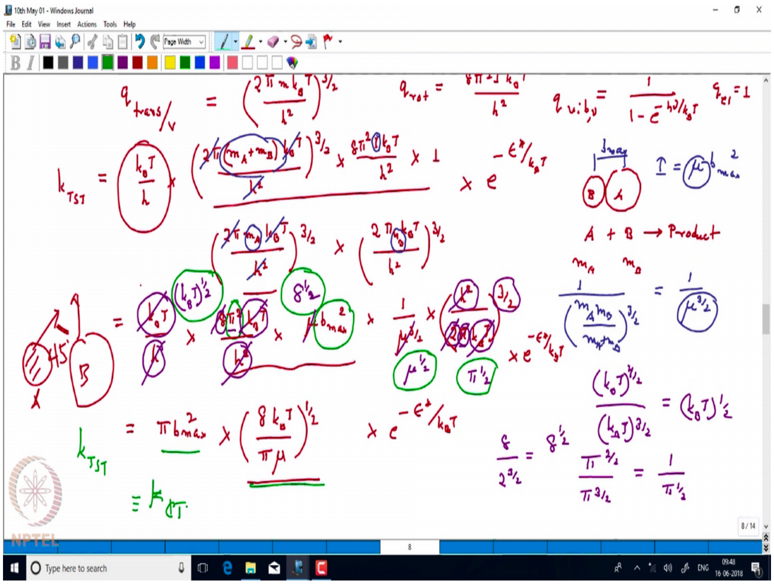

$q_{trans}/V = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$ $q_{rot} = \frac{8\pi^2 I k_B T}{h^2}$ $q_{vib,\nu} = \frac{1}{1-e^{-h\nu/k_BT}}$ $q_{el} = 1$

$k_{TST} = \frac{k_BT}{h} \times \frac{\left(\frac{2\pi(m_A+m_B)k_BT}{h^2}\right)^{3/2} \times \frac{8\pi^2 I k_BT}{h^2} \times 1}{\left(\frac{2\pi m_A k_BT}{h^2}\right)^{3/2} \times \left(\frac{2\pi m_B k_BT}{h^2}\right)^{3/2}} \times e^{-\epsilon^\ddagger/k_BT}$

b_{max} B A $I = \mu b_{max}^2$

A + B → Product

m_A m_B $\frac{1}{\left(\frac{m_A m_B}{m_A+m_B}\right)^{3/2}} = \frac{1}{\mu^{3/2}}$

45° A B

$= \frac{k_BT}{h} \times \frac{8\pi^2 k_BT}{h^2} \times \mu b_{max}^2 \times \frac{1}{\mu^{3/2}} \times \left(\frac{h^2}{2\pi k_BT}\right)^{3/2} \times e^{-\epsilon^\ddagger/k_BT}$

$(k_BT)^{1/2}$ $8^{1/2}$ $\mu^{1/2}$ $\pi^{1/2}$

$\frac{(k_BT)^{2}}{(k_BT)^{3/2}} = (k_BT)^{1/2}$

$\frac{8}{2^{3/2}} = 8^{1/2}$ $\frac{\pi^{2}}{\pi^{3/2}} = \frac{1}{\pi^{1/2}}$

$k_{TST} = \pi b_{max}^2 \times \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \times e^{-\epsilon^\ddagger/k_BT}$

$\equiv k_{CT}$

So, now we can proceed and then we can figure out what will be the expression for,, an bimolecular reaction what is the transition state theory expression for the rate constant for a bimolecular reaction and first thing first we have q A B dagger, we can actually look up who do not do remember it. So, it is cavity divided by h let me write it. So, you have k B T divided by h times we have translational partition function of the transition state divided by volume.

Now, the transition state, the way we are thinking right now is basically bimolecular reaction. So, the transition state in this case which is a bimolecular reaction will look like something like this or a you noted it as A and this is as V. So, it basically has many degrees of freedom, it has 3 translation, 1 vibration along the inter nuclear axis of these 2 hard spheres and then it has rotations, but it is a linear transition state, so, it will have 2 rotational degrees of freedom. And if you remember that the rotational partition function which we wrote that is basically for 1 degree of freedom, for 2 degrees of freedom we have to modify it accordingly.

And then it has 1 particular vibration and that vibration we can think that it is the reaction or in although this is not very correcting because you can you can imagine that I have a hard sphere at atom or molecule A and I have another hard sphere atom and molecule B and they are forming the transition state and there is some vibration I am saying, but it is not exactly the vibration along A B because that vibration will not give you reaction because it will just give a reaction where A and B are apart.

So, what are we saying is that it is a linear thing and there is some particular vibration that is giving me the reaction of the type A plus B is giving me product. So, that vibration we are basically isolating and that vibration is basically already less in the expression for the q A B dagger by V and we have a prime notation there and remember that is basically the prime takes into account of the fact that 1 degree of freedom is less and we are saying that particular degree of freedom is the inherent vibration which is leading to the reaction.

So, now we can proceed, now we see that the expression will be the first q it A B dagger divided by V. So, it has it is translational partition function which will be 2 pi m. Now if the mass of A is m A and mass of B is m B so, the as you can see the mass of the transition state will be m A plus m B because it will be the total mass, mass is conserved divided by h square which is a plant constant raised to 3 by 2 that is the q translation divided by V for the transition state times. I now have to write the rotations, rotational partition function and the rotational partition function in this case will be 2 I k B T by h bar squared, but we probably wrote the rotational partition function in terms of h.

So, we can actually instead of writing h, but we can write it as h square and h is h bar is h by2 pi. So, in the numerator will have 8 pi square I, we can use any of this expression and then this is for, a linear molecule ah. So, that is so, you had a sigma here and sigma is basically 1. And then what we have is 8 pi square I cavity by A square and then the vibrational, but the vibration we have already taken into account and then you have electronic which is just 1.

So, remember that since we have taken out the vibrational degree of freedom that is why it is giving my the k B T by h that expression and now I have the, q vibration q partition functions per unit volume for the reactants. So, first I will write it for A, now A has only translation and B also has a translation because this is a structure less atoms or molecules, their reactants. So, for A we can write it as 2 pi m A k B T divided by h square raise to the power 3 by 2 and for B we can write 2 pi k B T 2 pi m B k B T divided by h square raise to the power 3 by 2. And then in the overall expression we also have a

Boltzmann factor. So, where, the factor looks like it e to the power minus epsilon star by k B T and epsilon star is the 0 point energy difference between the transition state and the ground state for the composite ground state of the reactants.

Now, as we have to just simplify this expression as you can see here that is 2 pi k B T divided by h square, one of them will basically cancel with one of them in the numerator 2 pi k B T by h square that factor will cancel with one of them, let us say this gets cancelled with this. So, I mean I can actually use some other color. So, I am saying that that is getting cancelled and then I am left to it something like 1 2 pi k B T by h square in the denominator plus I have here m A m B and m A plus m B.

Now, those things we can actually arrange and we see here that is nothing, but 1 divided by m A m B by m A plus m B raised to the power 3 by 2. So, that is nothing, but the reduced mass as, we as it follows from the expression from the reduced mass. So, this is nothing, but 1 divided by mu to the power 3 by 2. Now this I is a basically moment of inertia and for this I of the transition state if we think that the distance is we already denoted it just b max. So, the moment of inertia is nothing, but mu b max squared.

So, we will replace that I as you will b max square and then what we are left with that this mu as you can see will basically cancel with the mu to the power 3 by 2 in the denominator. So, ultimately we will have a mu to the power half in the denominator and then you can also simplify with the other terms, we can actually quickly try, try doing that. So, have 1 k B T by h times, we will have I am writing the rotational partition function first, 8 pi square will have k B T divided by h squared and I am writing as mu b max squared that was the rotational partition function and then I have 1 over mu to the power 3 by 2 and X in the denominator I have 2 k B T divided by h square h to the power 3 by 2.

So, that I can write it as h squared in the above I can write to write it as h square and then I had 2 pi k B T raised to the power 3 by 2. So, they not let, let us all look at it like what gets cancelled with each other first thing first this mu gets cancelled with mu to the power 3 by 2. So, I have mu half here and then what we are left to it is let, let us first look at the h. So, I have h here, I have h here h square here. So, I have h q and then I have h square to the power 3 by 2. So, that is also h cube. So, these things actually gets cancelled with each other and then all I am left with is 2 pi k B T here and all I also have 8 here, but remember that that is raised to 3 by 2.

So, let us look at the cavity terms first. So, I have k B T here, I have k B T here. So, I have overall k B T squared and then in the denominator I have k B T to the power 3 by 2. So, k B T square you can think of it as k B T to the power 4 by 2 and divided by I have k B T to the power 3 by 2. So, that will give me basically 1 over not 1 over that will give me basically k B T to the power half. So, these things will get cancelled with this k B T and in the numerator I will have k B T to the power half.

And let us now look at the new pi. So, I have pi square here and I have pi to the power 3 by 2. Now I will just do a simple trick, what I am going to do here is that out of this pi square, I will actually keep one of the pi and associate with, with the b max. So, what I am doing here is that I have one pi here, I am basically writing this pi square as a pi in to pi and that 1 pi I am actually sitting with this b max. So, basically I have pi b max squared because I will show the equivalence of the condition state theory and the collision theory expression and I have a pi b max squared here as you can see here.

Now, then what I have is remember that I also have e to the power minus e star by k B T that and not touch. So, I will have 1 e to the power minus e star by k B T and then let us have a look what we are left to it. So, we are left with 1 pi here and so, we have 1 pi, let me use the different colors. So, you have 1 pi in the numerator and in the denominator we have pi to the power 3 by 2. So, that pi we can write it has pi to the power 2 by 2. So, half overall on over pi to the power half in the denominator. So, again so, this pi and one of this pi will get cancelled and then I will have pi to the power half in the denominator.

And let us now look at numbers like I have 2 here 2 to the power 3 by 2, I have 8 here. So, we can also have a look how it goes. So, I have h divided by 2 to the power 3 by 2. So, 2 to the power 3 by 2 is basically 8 to the power half. So, overall I will have 1 over not 1 over, I have this can 8 divided by square root of 8. So, I will have square root of 8 or 8 to the power half ah. So, this thing will get cancelled with this and I will have 8 to the power half.

So, now I can actually arrange the terms and as I can see here; so, I have 1 8 to the power half, I have 1 k B T to the power half and then I have 1 mu to the power half and pi to the power half. So, I just arranger all of them. And, then I can write it in the numerator, I have 8 k B T and that denominator I have pi mu everything raised to the power half. And, as you can see that this is exactly the expression for the relative average velocity which you have already figured out and that will be basically when the relative collision between A and B happens at a angle which is basically average of 0 and 90 degree; so, which is basically the 45 degree.

Now, as you can see that, now we have actually got that our collision theory rate expression that I have pi b max squared and then I have 8 k B T by pi mu raised to the power half, it is a average of the relative velocities and times this Boltzmann factor. So, now, we see that we can easily show that k T S T is equivalent to k C T or the collision theory. If we think that the reaction is happening due to collision or due to bimolecular collision between two structure less atoms or molecules.

So, this basically shows the equivalence of the 2 methods although at a first look at the collision theory rate expression and the transition theory rate expression look looks very - very different, but we see that for structure less atoms and molecules and the bimolecular reaction between them these 2 are very much equivalent. So, now, we will see, the thermodynamic aspect of the transition state theory.