Advanced Chemical Thermodynamics & Kinetics

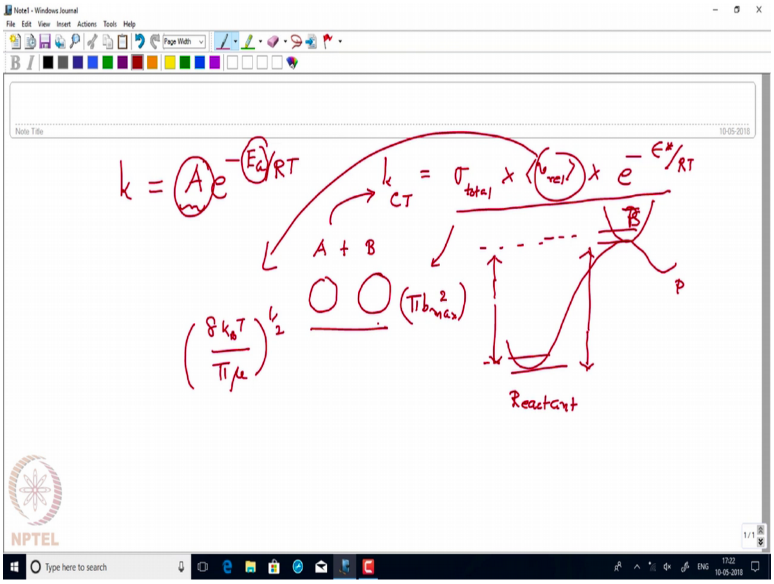
Prof. Arijit Kumar De
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture – 26
Introduction to bimolecular reaction dynamics 02

So, we have discussed about some introduction to potential energy surfaces and there we discussed that a point on the potential energy surface exists that is a saddle point. In the sense that along the reaction path there exist a maximum, but in all other direction sitting at the minima in the put in with respect to the I mean potential energy surface.

So, at that saddle point you can think that a transition state between the reactants and the products occur and what Henry Eyring and Michael Polanyi are good is that if we can study the statistical properties of this transition state, we can actually calculate the reaction rate.

(Refer Slide Time: 01:09)



Now, before we go through the details how what is the derivation of this transition state theory, let me give you and reminder that the rate constant is expressed experimentally which is the Arrhenius equation as this, e to the power of minus E a by R T, where A is known as the pre exponential factor. Now, we do not know Arrhenius actually did lot of experiments and from that he figured out this empirical relationship and where this E a he said it is a minimum energy required to for the reaction to occur that is known as a activation energy.

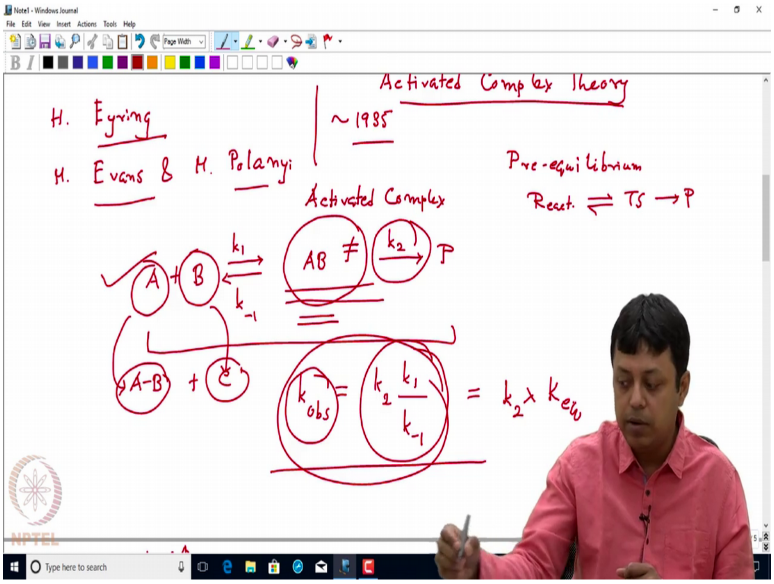
Now, A is the pre exponential factor and we will calculate A here and also just to remind you that from collision theory we already found which we did not derive in this course which is derived in the earlier version of this course is that in collision theory expression, it will be something like the total cross section times the average of the relative velocity times e to the power minus E star by RT. So, where E star is the minimum energy in the potential energy surface that we cross.

Now, there is a difference between E star and E a. E a is a experimentally determined quantity and E star means, if you have reactant to product going like this, so, E star classically means this difference in this minimum energy that you require from going from reactant to products this is the product reactant to the say transitions through the transition state.

Now, in this case which you will see that we can actually think in a more rigorous way that both the reactants as well as the transition state has some vibrational structure and in that case actually the E star denote the difference in the zero point energies. So, that correction will met here, but whatever is the situation for a two body collision like A plus B, where A and B are structureless, it should give me back to the collision theory rate expression provided the A and B are kind of structure less hard sphere.

So, under hard sphere approximation remember we got this relationship or sigma total is again pi b max squared, where b max is the addition of the radius of the two bodies and pre relative also has a expression and average velocity expression is 8 K B T by pi m and since it is a relative velocity we have to replace m by mu raised to the power half. Now, we should get back this expression if we use the transition state theory and if we apply the condition of hard spheres. Now, let us proceed.

(Refer Slide Time: 04:16)



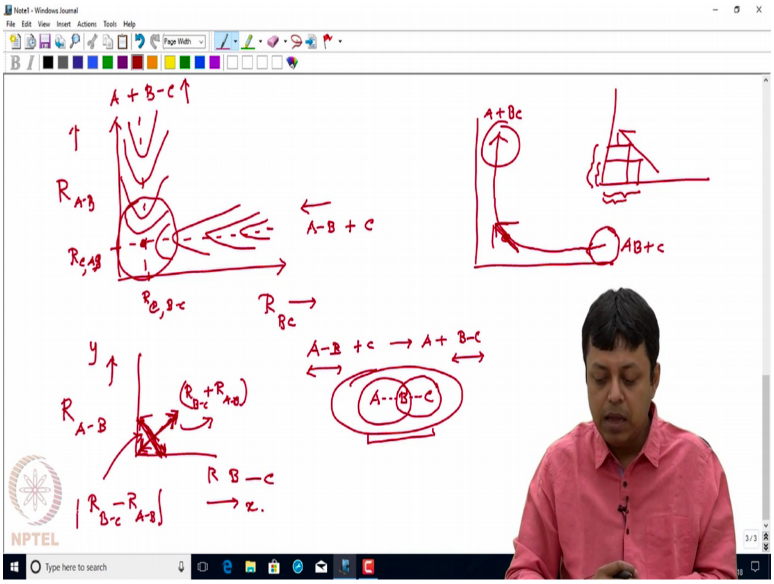
So, what Henry Eyring and Evans and Polanyi Henry Eyring and Meredith Evans and Michael Polanyi proposed around 1935-37 is that the transition state exist which they denoted as say A B dagger for a bimolecular reaction between A and B and they assumed that this transition state is basically in equilibrium with the reactants which are the two molecules and then eventually the transition state forms product.

So, this kind of equilibrium is very known to you which already discussed when we discuss the pre equilibrium or equilibrium approximation. So, they said that there is a pre equilibrium that exists between the reactants and transition state and then the transition state forms the product. Now, for if we assume that thing then we can actually right away apply the equilibrium approximation which we had already done and we know how to do it. Secondly, what is this rate of product formation?

Now, you know that this equilibrium approximation will hold if this step the k 2 is very slow or the second step or the step of the product formation is much slower. Now usually; that means, that whenever I form a activated complex according to their nomenclature this is called as Activated Complex. So, this activated complex which we are denoting as A B dagger in a third bracket and this activated complex we can actually remove the bracket right now because usually we are using the bracket notation for the concentration.

And so they said that this A B dagger is a very very short lifts phases and then once it vibrates along the a particular degree of freedom which is along the reaction coordinate each vibration will give me a reaction. Now, what does it mean? Let us actually go back to our discussion on atom diatom collinear reaction and try to actually explain it what do you mean by this vibration of this A B dagger ok. Now, for that let us try to draw the 2 dimensional contour diagram of potential energy surface once again.

(Refer Slide Time: 07:05)



Now, suppose again I am plotting the A B distance along this direction and B C distance along this direction or maybe we can actually do the reverse, it will be clear why I am doing the reverse thing. And the B C distance we can plot along say x axis and along the y axis I am plotting the AB distance.

So, around here when the A B distance has the equilibrium bond vibration, equilibrium bond vibration for A B, so, this position corresponds to basically a stable A B molecule plus a C is attacking. Similarly along B C if, I say that this is the equilibrium distance our equilibrium for B C bond, so, this position denotes somewhere where I have the B C molecule and plus the A atom something like that.

Now, where we are starting? We are starting from say here, this is our reactant and this is our product. So, we can actually draw I mean very schematically the potential very qualitatively the potential energy surface. So, again these lines actually corresponds to at the energies are same, these are isoenergetic surfaces and then there is a barrier along the reaction coordinate.

Now, is if you look at this region when actually we are crossing the transition state, how the motion looks like? So, as I have drawn here I have A B plus C here and I have A plus BC here. So, the path will be something like it is rising and then crossing at the barrier and it is reaching here. So, this path is something like this, right here; what is the kind of motion it has? As you can see it has to move the reaction if it has to move it is moving kind of diagonally.

Now, what is this motion let us think about it. Now, what are the coordinates here? So, in the x axis we have plotted B C vibration, in the y axis we are plotting A B vibration. So, think about it like I had initially two vibrations. So, the stretching of this A B plus C and in the final product region I have basically A plus B C and I have the stretching vibration for the B C. So, which are actually vibration for this zone and this zone ok, but near the transition state actually I have something like a structure like this A B C, it is a collinear atom diatomic molecule again. And again remember that this is neither being broken and this is neither being formed, it is actually in between.

Now, this complex which they called as Activated Complex has now two bonds. So, similarly if you do a normal mode analysis you can actually expect to vibrations one is symmetric vibration, one is anti symmetric vibration. Now what is symmetric vibration? Symmetric vibration means both the A B and a B C actually stretches simultaneously.

Now, here is the beauty. So along this direction along say x direction, I have B C vibration, along y direction I have A B vibration. So, along the transition state I am saying that it is neither x or y vibration, but rather a vibration which is along this. If I move along this as you can see both the A B and B C are stretching to the same extent.

Something like you had a coordinate system like x and y and I am converting this coordinate system into a new coordinate system, where actually I have x plus y, something like that where both the x and a y are simultaneously varying. So, this is nothing but the symmetric stretch and then I can also think about another a motion orthogonal to it which is the asymmetric stretch because if you think that the molecule is vibrating along this direction; A B A B molecule is vibrating. So, what will happen?

So, this vibration means if you can think that I have a rectangle like this and I am vibrating along this rectangle which is this direction. You can instead of x plus y, we can actually write it as something like in our original notation which is R B C plus R A B which is the symmetric stretch.

So, it is moving like this, but the reaction happens as we saw along this direction. So, that is an asymmetric coordinate. Why? Because as you can see if I move along like this if I draw it once again if I move along like this, so, if I keep on moving as you can see that this distance is shortening, but this distance is increasing. So, this is the asymmetric vibration that gives you the product and it is which is very obvious because you had A B C something like that. If you symmetrically vibrate nothing happens, but if you asymmetrically vibrate, so, at the B C bond compresses and the A B bond stretches. So, that stretching will lead to a breaking of the A B bond and formations of the B C bond something like that.

So, those kind of vibrations are actually the asymmetric stretch vibration of the A B C molecule. So, basically what we said that the A B C has sets of vibration which cannot be explained like just a B C vibration or just a A B vibration which has basically a combination of A B vibration and B C vibration which gives rise to the normal modes and that is the meaning of normal mode. You do not have actually isolated A B vibration or B C vibration. You can think of the entire problem like the A B and B C both are vibrating together, but whether now they are vibrating together in a symmetric fashion or in phase or they are vibrating in an anti symmetric fashion or in an outer phase way.

So, this coordinate is nothing but something like R B C minus R A B. So, it is nothing but a kind of coordinate transformation at the transition state because as you can see from the geometry in the transition state you diagonally cross the potential energy surface you have to cross it because you are vibrating like here as A B and then you have to vibrate like here as B C. So, you have to somehow cross the trajectory has to cross diagonally.

Now, the question put Eyring and Polanyi and Evans, they asked is that if I have this kind of situation then I can actually apply statistical mechanics to understand what is the frequency of this vibration and what are the statistical properties of this vibration. From this very fundamental assumption that there exists a free equilibrium and since we are talking about all the statistical properties of this molecule which is A B dagger again do not confuse with A B dagger in our like here actually I am talking about bimolecular collision and we already talked about atom diatomic collision which is something like this. So, the A in our notation can represent A B, the B in our notation can be represents C something like that.

So, this together right now I am writing as A, this I am writing has to B something like that. It may be two diatomic molecules also, it may be two polyatomic molecules, it does not matter that is why I am just using A B notation. So, there is no inherent assumption that how big is the molecule is just a bimolecular collision and all of you know that fundamentally these elementary reactions are mostly bimolecular in nature because for unimolecular reaction also there is a bimolecular reaction that precedes the unimolecular reaction. So, bimolecular reactions are at the hard to understand chemical reaction dynamics.

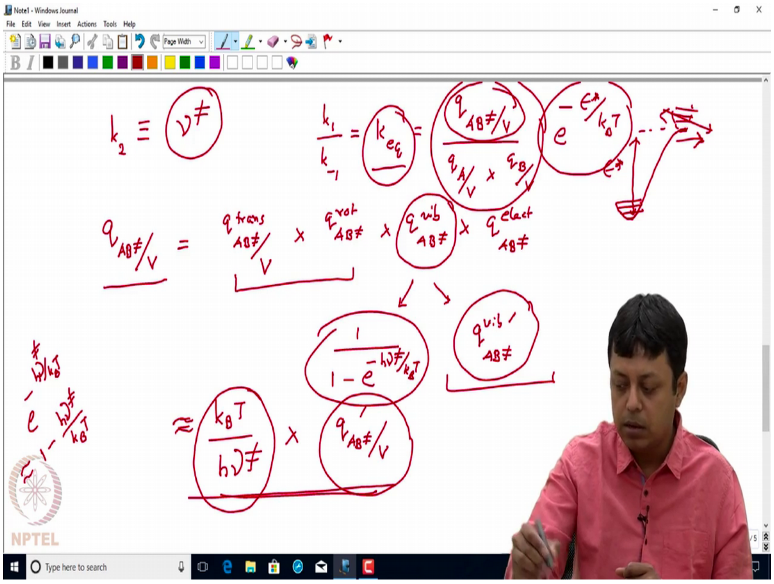
Now, since we are talking about this activated complex of the two molecules we call this version of transition state theory as activated complex theory. And again it was put forward by Henry Eyring Meredith Evans and Michael Polanyi. Now, what will be the rate constant if I actually applied the pre equilibrium condition? Now all of you know that we have already derived it the observed rate law will be nothing but a combination of rate law which will be k 2 k 1 by k minus 1 already we showed it. So, according to Eyring and Polanyi what we have to now calculate is this in terms of this rate constant can we actually get some other parameters with which we can actually calculate the observed rate law?

Now, what is k 2? k 2 is the frequency at which the transition state breaks into the product. So, the idea is that here we are talking about only A plus B, two product irreversible reaction. So, here the assumption here is that I had an A B C adduct and if in at a transition state and then it can vibrate symmetrically that will not give me reaction because that motion is orthogonal to the product formation. So, if it vibrates like this so nothing will happen. So, the it will not give me the reaction.

So, it is a stable vibration of the transition state; however, it if it vibrates asymmetrically, it can now you can argue always that it can vibrate asymmetrically, something like the B C bond is stretching and then again C will fall apart then actually we will go back to the reactant side. So, that is why I am saying that it is kind of in equilibrium with the reactant also, but if it vibrates in the other way meaning the A B bond is stretching too much then actually it will fall apart the A and B fall apart and the BC will form.

So, the assumption here is that part vibration of this asymmetric vibration if it goes in favor of the product side, it will give me a product or if it gives me if it is something like that the B C bond is stretching too much it will give me the reactant. So, it will survive only over the time period of this asymmetric stretch vibration for a collinear atom diatomic reaction, but for in general case they said that there will be one particular vibration if it vibrates once it will immediately form either the reactant or the product.

(Refer Slide Time: 18:44)



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

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

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

$$q^{vib}_{AB^{\neq}} \rightarrow \frac{1}{1-e^{-h\nu^{\neq}/k_BT}},\quad q^{vib\,\prime}_{AB^{\neq}}$$

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

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

So, the frequency of the reaction which is the k 2 is nothing but identical to a particular characteristic frequency, which is along the reaction Corinne and that frequency let us denote it as nu dagger. Now, k 2 is a rate constant which is a bimolecular rate constant, the overall bimolecular rate constant is given by k minus 1 into k 2. And nu dagger if you remember that has a unit of second inverse. So, we can actually approximate new dagger you can say that new dagger also has a dimension of a rate constant.

Now, what we are saying here is that fine. So, that is the value of k 2 and what about k 1 by k minus 1? Now already we know that k 1 by k minus 1 is nothing but an equilibrium constant, the equilibrium between the reactants and the transition state. Now, from our previous classes on statistical thermodynamics we know that I can write the equilibrium constant in terms of the molecular partition functions of the reactants and the products.

So, it will be partition function of the products first. So, the product I denote it as q A B dagger. Remember it is actually the partition function per unit volume and divided by the partition function per unit volume for the reactants. So, in this case it will be something like this and times I have a factor where this E star denotes the differences in the zero point energies of the reactants and the transition state; that we also discussed.

So, in the equilibrium constant when I discussed about A and B are in equilibrium where, A and B are both molecular spaces there we said that it would be the zero point energy difference in this case it is the zero point energy difference between the reactants and the transition state. So, the reactant has some vibrations and the transition state also has vibration but remember that these vibrations are orthogonal to the trajectory because along this direction if it vibrates it will just fall apart. So, right now I am talking about all vibrations in the transition state. So, this zero point energy difference is the E star here.

Now, think about it, among this q the partition function for the transition state which you denote as q dagger by A B, so, it contains translation rotation vibration as well as electronic partition functions. Now, we can write it as so it will be composed of something like q translation of the A B dagger. Usually we associate at the volume with q translation, it will be times these q rotation of A B dagger then it will have q vibration of A B dagger and then there will be also electronic, but usually in this case I will say that electronic partition function of is 1, but we are just skipping it for the time being.

Now, you can think among all this vibration one vibration is along the reaction coordinate along this arrow and all other vibrations are orthogonal to this reaction coordinate. So, we have to we can actually split this vibration into two parts where we will calculate one vibration, one vibrational partition functions for that particular vibration which has a frequency nu dagger because nu dagger is along the reaction coordinate. Now, what is the expression for vibrational partition function? It is 1 by 1 minus e to the power minus h nu by k B T; 1 minus e to the power minus here it will be h nu dagger for that particular partition function and the rest of the thing I am just writing it as q vibration by A B dagger and I am using a prime notation.

This prime means it is basically the partition function, vibrational partition function except 1 degree of freedom. Which degree of freedom? That degree of freedom which is along the reaction coordinate and which has a characteristic frequency which is nu dagger. Now, what we are going to do? We are going to collect all these terms together and write basically q the entire thing I am writing it as q A B dagger by v prime times this particular term which we separated out.

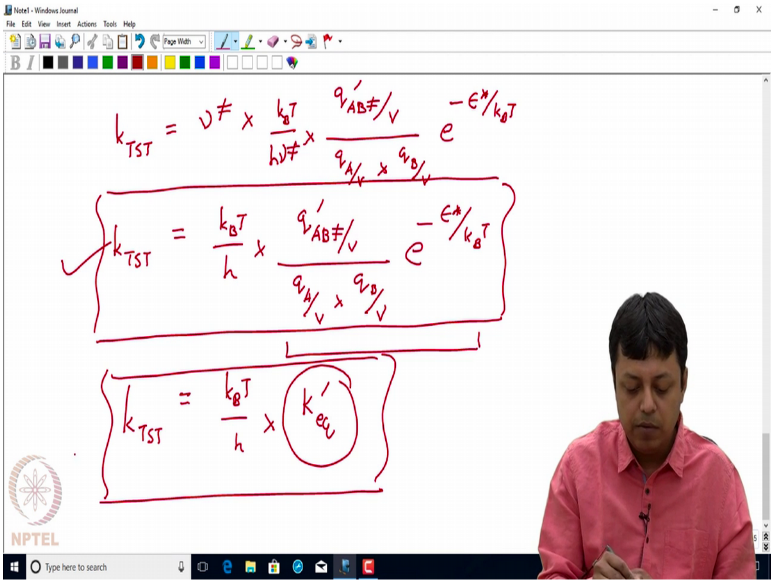
Now this can be evaluated very easily. How? Because I have E to the power minus h nu by k B T. So, that we can expand as 1 minus h nu dagger by k B T. Now, why I am truncating up to it is a series expansion up to the second term? The reason is as I said that this nu dagger is a low frequency vibration. Why? Because I said that for the equilibrium approximation to be valid, the k 2 at the rate of product formation has to be slow.

So, it is not very surprising also because you can think that this is an asymmetric stretching vibration which is has a much slower frequency and once it vibrates it is it fall separate. Now that is why this nu dagger or h nu dagger is much smaller compared to the k B T which is the thermal energy and then we say that ok. So, we can actually ignore the higher order terms. A moment you make this approximation this entire thing it is 1 minus e to the power minus h nu by k B T that actually becomes 1 over h nu by k B T or the entire thing becomes k B T by h nu dagger.

So, we see that the this partition function for the activated complex which is the A B dagger has a form of k B T by h nu dagger times all other partition function together which you can calculate of course, using statistical mechanics. And we will give you an example where we will calculate and but there is 1 degree of freedom less, which degree of freedom that by particular vibration which is along the reaction coordinate and which is much of slower frequency and which is have characteristic vibration of nu dagger.

Now, we can put back this into the equation. So, the original equation if you remember we had the observed rate which is k 2 by k 1 by k minus 1. So, for k 2 and replace it directly with nu dagger.

(Refer Slide Time: 26:01)



$$k_{TST} = \nu^{\neq} \times \frac{k_BT}{h\nu^{\neq}} \times \frac{q'_{AB^{\neq}}/V}{q_A/V \times q_B/V}\, e^{-E^*/k_BT}$$

$$k_{TST} = \frac{k_BT}{h} \times \frac{q'_{AB^{\neq}}/V}{q_A/V \times q_B/V}\, e^{-E^*/k_BT}$$

$$k_{TST} = \frac{k_BT}{h} \times K'_{eq}$$

So, what we get from the transition state theory is that it is k 2, k 2 is nothing but nu dagger time's k 1 by k minus 1, but k 1 by k minus 1 was connected to the equilibrium constant which is connected to the this combination of these partition functions times this exponential part and among this I replaced this part which is q A B dagger by v by this expression k B T by h nu. Let us just put it put all things together. So, I had the partition function of the products which is q dagger by v, but then we took out one particular degree of freedom that is why I am putting the prime thing, for the reactants we did not do anything.

So, it is q A by v q B by v these are all partition functions times e to the power minus E star by k B T and then that extra degrees of freedom we got the value as k B T by h nu dagger. As you can see the k B T will now get canceled out and then what will be left to it is the famous iodine equation which is k B T by h into q A B dagger divided by v q A by v into q B by v into e to the power minus E star by k B T.

So, this is the expression for the transition state rate constant and it has right now has no similarity with the rate constant which we got from collision theory. Now, we will see that these two are equivalent, but before that we will do one more thing. So, we can actually again remember that we wrote it in terms of the equilibrium constant.

And then we can again write this entire thing as an equilibrium constant in the sense that it is something like k B T by h. But this equilibrium constant is slightly different it is not exactly the same equilibrium constant for the transition state, but it is the equilibrium between reactant and a transition state, but with 1 degree of freedom less. So, that is why I am putting it as a prime sign ok.

So, you can actually look at it look at the similarities between this equation. So, initially I had it is nothing but k 2 into k equilibrium from this equation. So, we had k 2 into k equilibrium, where the equilibrium is between the reactants and the transition state. And now I cleverly actually have taken out 1 degree of freedom which is along the reaction coordinate because I expressed it in terms of the partition function, took out that degree of freedom, again recombine the partition functions and again writing this entire thing as a equilibrium.

But this equilibrium is not exactly the special it is a special equilibrium it basically does not have one particular degree of freedom. Now, this expression also will be useful for a discussing some important factor which we will be we will see soon. First we will see how what will be the expression for the transition state theory for a bimolecular reaction where the molecules are structureless.