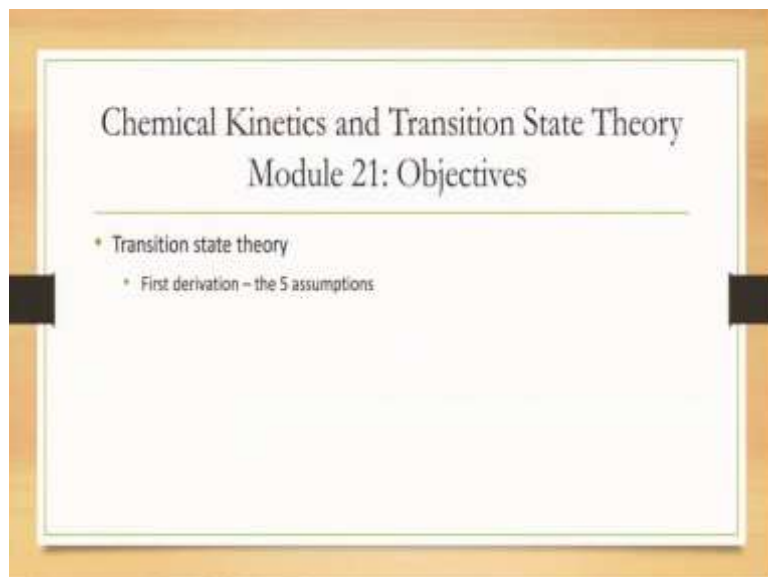


Chemical Kinetics and Transition State Theory
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Lecture 21
Transition State Theory: Derivation 1

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Hello and welcome to Module 21 of Chemical Kinetics and Transition State Theory. And today is the day we will finally derive the rate expression for transition state, we have looked at, we have done all of our prerequisites now, we have went through the statistical mechanics of partition functions.

And in the last module, we derived an important expression for how we calculate rates in a more general sense, we were thinking of a sample problem in some example of cars, but it is the same idea we hold for molecules as we will show to today. So, what we are following is the Laidler's book chapter 4 third edition.

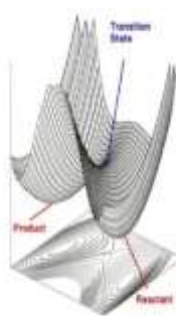
The proof that I am providing you today was originally derived in 1935 in two papers almost simultaneously, one was by Eyring and the other one was by Evans and Polanyi, the credit for this proof is given to these 3 authors.

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Recap

Transition state is the **maximum** energy structure along the reaction coordinate

Along any direction perpendicular to the reaction coordinate, T.S. in the **minimum** energy structure

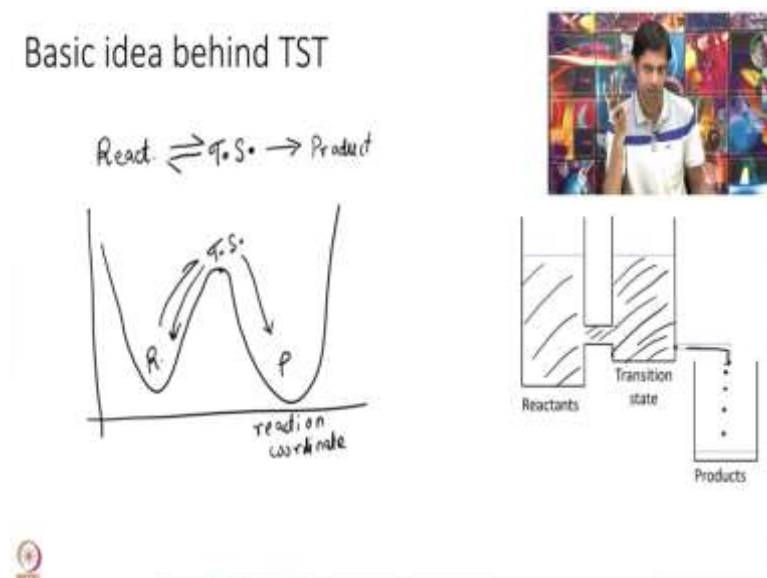
$$K_{eq} = \frac{q_P^0}{q_R^0} e^{-\Delta E_0/k_B T}$$
$$\text{Rate} = \int_0^\infty du D \rho(u) u$$


So, just a quick recap of several modules, the essence of several modules. First, what is a transition state that we described 2 modules ago. Transition state is the maximum energy structure along the reaction coordinate, reaction coordinate is the minimum energy path joining reactants and products by go from reactant to product in the minimum energy fashion and the maximum energy point along this path is called a transition state.

The major confusion that I have seen with many people transition state is not the global Maxima of the potential energy along every coordinate perpendicular to the transition state, transition state is a minimum. So, I have given you a sample potential energy surface here, this is reactant, this is product. If I go from reactant to product, the maxima that will occur here will be the transition state, but if I you think of drawing a line which is perpendicular here, you see there are other points on the energy surface which are more than transition state.

We derived another very important expression a few modules ago, which told us how we calculate equilibrium constant given here, and q_P^0 and q_R^0 our partition functions per unit volume and divided by Avogadro number if you are interested in moles units, and in the last module, we derived the expression that rate is integral over speeds D which is a density overall density ρ is the probability of having at speed u into u and u is basically the flux.

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So, what is the basic idea behind transition state theory, what are we doing? What are we doing essentially is you have a reactant and you have a product and in between we postulate that a transition state exists and we postulate that this reactant and transition state are at equilibrium and from transition to product is one way.

So, we think of it in this language that you have a surface like this; you have this as the reactants it this is essentially just the reaction coordinate. This is product and in between at the maximum energy so, it is the transition state we have an equilibrium between transition state and product and the transition state is falling to products. What I usually think at least in my head is the following. Imagine reactants is one big jar of water. So, I have some water here filled here.

And transition state is just another beaker which is raised in height, and it is connected with my reactant states very strongly, so we have a big gap here that connects it. So, basically transition state is in equilibrium with your reactants. But with lesser water, because it is its height is higher and we have a small hole in my transition state here.

So, that water is slowly trickling out drop by drop. And this is only one way the well of products does not affect my equilibrium of reactants and transition state at all. Of course, it is an assumption, but this is the assumption under which transition state theories derived, we

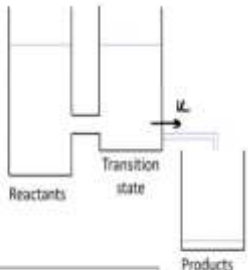
will over time think about these assumptions very carefully, but for now, let us make these assumptions let us assumed that the flow from transition state to products is very slow.

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Basic idea behind TST

$$\text{Rate} = \int_0^{\infty} du D \rho(u) u$$

u = speed
 D = density of particles at transition state
 $\rho(u) du$ = fraction of particles at transition state with speed u



Assumption 1: Transition state exists
 Assumption 2: Classical treatment of nuclei
 Assumption 3: No re-crossing; i.e. particles do not come back from product well

So, we essentially use the rate as we had discussed in the last module. So, the rate is nothing but if I sit at the transition state then the rate is nothing but the speed at which I am crossing the transition state the dens... multiplied by the density of the transition state and the density of the transition state is nothing but that dense... total density of particles at a transition state multiplied by the fraction of particles having speed u .

Obviously, you can go back one module and look at it again that was a very important module in which how we discuss how we calculate this rate expression. So, today we will make things a little bit more mathematical a little bit more concrete in writing this rate expression, I have actually made 3 assumptions. So, let us be very clear on what our assumptions of our theory are.

The first assumption that we make is the transition state exists nobody tells it that it has exists. Actually, there are reactions for which transition state does not exist, but we are only considering those problems where a transition state exists. Second, we are thinking of a classical treatment, we are thinking of particles moving at speed u which is a very Newtonian notion.

And the third thing is we are looking at only positive speeds the integral if you see here is from 0 to infinity we are not we are imagining this picture where you start with the

transitional state and if you cross the transition state to product you do not come back. So, these are 3 important assumptions we have already made while writing this expression.


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Density of particles per unit length

Assumption 4: Transition state is in thermal equilibrium with the reactants

$$K_{eq} = \frac{q_P^0}{q_R^0} e^{-\Delta E_0/k_B T}$$

$R \rightleftharpoons T.S.$
 $K_{eq} = \frac{q_{T.S.}^0}{q_R^0} e^{-E_0/k_B T} = \frac{[T.S.]}{[R]}$



$Rate = \int_0^{\infty} dx D p(x) u$

So, we will move forward and we have to now calculate these 2 quantities D and rho. If I calculate this then I will do this integral and I am done fine, we will start with this density of particles per unit length and for that I will be using this relation that we had derived earlier of equilibrium constant relating with partition functions, so our basic idea of transition state is that the reactant is in equilibrium with transition state.

So, that is our assumption number 4 that the transition state is in thermal equilibrium with the reactants. If this is true, then the key equilibrium of this transition between R and TS can then be written as q_R naught and this so again my 1D picture, this is your E naught, I will skip this delta from now on just to make my own life easy. I will just write it as E naught as the activation energy.

So, remember this expression I am using between transition state and reactant not between product and reactant, product and reactant or not at equilibrium, transition state and reactant are in equilibrium. So, this E naught is the energy difference between transition state and reactant which is called activation energy, we have something we are making some progress. And key equilibrium is given by transition state divided by reactant concentrations that is the definition of equilibrium constant.

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Bimolecular transition state theory

$$A + B \rightleftharpoons \text{TS} \rightarrow \text{Products}$$

$$\frac{[\text{TS}]}{[A][B]} = \frac{q_{\text{TS}}^0}{q_A^0 q_B^0} e^{-E_0/k_B T}$$

$\text{Rate} = \int_0^\infty dx D p(x) v$

What we are going to do is for now at least, limit ourselves to a biomolecular theory. So, we have only A plus B going to transition state going into products. So, what we get is transition state divided by concentration of reactants becomes concentration of A into concentration of B, this is equal to q transition state naught divided by qA into qB.

That is how we find partition function of several molecules, we multiply them together into e to the power of minus E naught over DB. So, I am doing a simple thing, I am just translating reactants to A and B, nothing more, nothing complex.

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Density of particles per unit length

Assumption 5: At the transition state geometry, Hamiltonian is separable

$$[\text{TS}] = \frac{q_{\text{TS}}^0}{q_A^0 q_B^0} e^{-\frac{E_A}{k_B T}} [A][B]$$

$$H_{\text{r.s.}} = H_A + H_{\text{TS}}$$

$$q_{\text{r.s.}}^0 = \frac{1}{V} \sum_{\text{states}} e^{-\beta E_i} = \frac{1}{V} \sum_{\text{states}} e^{-\beta E_A} \sum_{\text{states}} e^{-\beta E_{\text{TS}}} = \frac{q_A}{q_{\text{TS}}} q_{\text{TS}}$$

$$q^{\ddagger} = \sum_{\text{states}} e^{-\beta E_i} \quad ; \quad q_{\text{TS}}^{\ddagger} = \sum_{\text{states}} e^{-\beta E_{\text{TS}}}$$

<https://pubs.rsc.org/en/content/articlehtml/2016/sc/c6sc01066k>

So, I have taken A and B and I have put it on the other side. Now, we will make our final assumption of our theory. The final assumption in our theory is at the transition state geometry, Hamiltonian is separable. What I mean by that, so you have this reaction coordinate, going like this. So, this is a zoomed in picture, close to transition state.

So, I call this reaction coordinate q , and I call up perpendicular coordinates to this reaction coordinate as something perpendicular. And you have many, many coordinates that are perpendicular in drawing, I can draw only 1. But you can imagine I have n number of coordinates $3n$ number of coordinates actually, out of which only one coordinate is reaction coordinate, and $3n$ minus one of them are perpendicular coordinates.


So, the final assumption I am going to make is that Hamiltonian, add the transition state is Hamiltonian along q plus Hamiltonian along perpendicular coordinates. So, my q_T is naught, which is nothing but 1 over volume, the partition function which is sum over, let us say, a states i . So, we play the same trick as we have done a few times we divide these states into q and perpendicular coordinates, q states and perpendicular states.

And I am going to call this thing as q_{TS} . And this thing, I will just give a notation, so I am going to call this q_{TS}^\ddagger . Actually, this divided by volume, so I take this volume, and I put the volume here. So, my q_r is just sum over q states. And q_T^\ddagger is dagger is sum over all other coordinates, all other states. But this is an assumption. But I can separate it, but it is a reasonable assumption to make, that at the transition state you can separate things out.

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Density of particles per unit length

Assumption 5: At the transition state geometry, Hamiltonian is separable



$$[TS] = q_r \frac{q_{TS}^\ddagger}{q_A^0 q_B^0} e^{-\frac{E_A}{k_B T}} [A][B]$$

$q_r = \int_{-\infty}^{\infty} \delta(q - q_{TS}) dq$
 $q_r = \int_{-\infty}^{\infty} \delta(q - q_{TS}) dq$
 $q_r = \frac{L}{h} \sqrt{2\pi k_B T m^{TS}}$

$$D = \frac{[TS]}{hX} = \frac{\sqrt{2\pi k_B T m^{TS}}}{h} \frac{q_{TS}^\ddagger}{q_A^0 q_B^0} e^{-\frac{E_A}{k_B T}} [A][B]$$

$q_r = \frac{L}{h} \sqrt{2\pi m k_B T}$

So, I made this I have divided my partition function of transition state into two terms. So, I get the following expression here. What about it? Now, we estimate, what is our q_r ? So again, think of this transition state, you have this transition state sitting here, it is a zoomed in picture and q_r is the transition partition function corresponding to motion along the reaction coordinate.

So, q_r is partition function along 1D partition function along reaction coordinate. So, we estimate that as a 1D translational partition function. So, this is nothing but we are just going to use the classical version of it, due to the power of minus beta half $m u^2$. So, I am supposed to write $e^{-\beta H}$ the power of minus beta Hamiltonian, but my Hamiltonian along speed is simply half $m u^2$, and integrate over all speeds, this is your partition function along r .

But if you remember sorry and I also have along x some length. So, if you remember we have already derived this expression before. So, you can go back a few modules and we had derived the classical partition function for translation and so, this is equal to nothing but LX over $h \sqrt{2\pi k_B T / m}$ and so, the m here is m of transition state.

So, let me make that very clear, this is the mass of transition state what we estimate my D as nothing but the concentration of transition state per unit length. So, remember what was D ? D was the density of particles per unit length here we need concentration because that is the language in which rate of reactions working, it is rate of change of concentration. So, that is why we just have a concentration per unit length, but fundamentally nothing different.

So, this becomes equal to I will substitute this q_r here and divided by $LX \sqrt{2\pi k_B T / m}$ transition state divided by $h q_{\text{transition state}}$ or $q_A \text{ naught } q_B \text{ naught } e^{-E_A / k_B T}$ into concentration of A into concentration of B . So, I have made the first thing now I have got the density of particles per unit length to be more accurate it is density of concentration because rate works in the language of concentration. So, just a minor change of language essentially per unit mole per unit volume that is all.

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Calculating $\rho(u)du$

Assumption 4: Transition state is in thermal equilibrium with the reactants

$$\rho(u) du = N e^{-\frac{\beta}{2} \frac{m u^2}{\tau}}$$

1D

$$\int_{-\infty}^{\infty} du \rho(u) = 1$$

$$\int_{-\infty}^{\infty} du N e^{-\frac{\beta}{2} \frac{m u^2}{\tau}} = 1$$

$$N \cdot \sqrt{\frac{2\pi m \tau}{\beta}} = 1 \Rightarrow N = \sqrt{\frac{\beta \tau}{2\pi m}}$$

$$\rho(u) du = \sqrt{\frac{\beta \tau}{2\pi m}} e^{-\frac{\beta}{2} \frac{m u^2}{\tau}}$$

Useful integrals:

$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

So, let us do the final thing and calculate our density as well and rho u du again is the density of particles at speed u fraction of particles at speed u but we know how to do that that is the Boltzmann distribution. So, we have been looking at it in great detail and this is again one-dimensional density. So, let me emphasise that by writing 1D very very clearly, this is nothing but e to the power of minus beta half mu square into normalisation constant.

And once more in doing so, we are making the assumption the transition state is at thermal equilibrium. It may not be in reality, but it is an assumption. So, that is we can calculate this n very easily. How do I calculate n? Well, we integrate over all possible speeds this should be equal to 1 we have done these kinds of integrals a few times.

So, this is equal to root of 2 pi M over kBT. So, we get n is equal to, so this integral is again a gaussian integral gaussian integral is provided here. If I substitute the value of a, I can calculate the integral. So, finally the rho of u du is equal to root kT over 2 pi m e to the power of minus beta half mu square.

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Transition state rate

$$\text{Rate} = \int_0^{\infty} du D \rho(u) u$$

$$D = \frac{\sqrt{2\pi m^{\ddagger} k_B T} \frac{q_{\ddagger}}{q_A q_B}}{h} e^{-E_A/k_B T} [A][B] \quad \checkmark$$

$$\rho(u) du = \frac{m^{\ddagger}}{\sqrt{2\pi k_B T}} e^{-\beta \frac{1}{2} m^{\ddagger} u^2} \quad \checkmark$$

$$= D \int_0^{\infty} \frac{m^{\ddagger}}{\sqrt{2\pi k_B T}} e^{-\frac{\beta}{2} m^{\ddagger} u^2} u du$$

$$= D \frac{m^{\ddagger}}{\sqrt{2\pi k_B T}} \int_0^{\infty} e^{-\frac{\beta}{2} m^{\ddagger} u^2} u du$$

$$= \frac{1}{2} \frac{\beta m^{\ddagger}}{2} = \frac{D (k_B T)^{\frac{1}{2}}}{\sqrt{2\pi m^{\ddagger} k_B T}} \quad \text{D} \sqrt{\frac{k_B T}{2\pi m^{\ddagger}}}$$

$a = \frac{\beta m^{\ddagger}}{2}$
 Useful integrals
 $\rightarrow \int_0^{\infty} dx x e^{-ax^2} = \frac{1}{2a}$

Calculating $\rho(u) du$

Assumption 4: Transition state is in thermal equilibrium with the reactants

$$\rho(u) du = N e^{-\frac{\beta}{2} m^{\ddagger} u^2}$$

$$\int_{-\infty}^{\infty} du \rho(u) = 1$$

$$\int_{-\infty}^{\infty} du N e^{-\frac{\beta}{2} m^{\ddagger} u^2} = 1$$

$$N \cdot \sqrt{\frac{2\pi m^{\ddagger}}{\beta}} = 1 \Rightarrow N = \sqrt{\frac{\beta}{2\pi m^{\ddagger}}}$$

$$\rho(u) du = \sqrt{\frac{\beta}{2\pi m^{\ddagger}}} e^{-\frac{\beta}{2} m^{\ddagger} u^2}$$

Useful integrals
 $\rightarrow \int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}}$

So, now we have the two expressions of D that I calculated couple of slides ago and we have for rho and once more I think I had in the slide I had forgotten to write m as m TS, so let me get back and correct there. All the masses here are at the transition state, so that we have to be careful about in labelling. So, now we had a value of D and we have a value of rho and we just put it in this integral that is all.

So, D does not depend on u at all. So, I can take it out to set the integral. I have some normalisation constant into rho a few e to the power of minus beta half m TS u square into u I think I have made a little mistake in calculating transition state in the normalisation constant.

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Calculating $\rho(u)du$

Assumption 4: Transition state is in thermal equilibrium with the reactants

$$\rho(u) du = N e^{-\frac{\beta}{2} m u^2}$$

$$\int_{-\infty}^{\infty} du \rho(u) = 1$$

$$\int_{-\infty}^{\infty} du N e^{-\frac{\beta}{2} m u^2} = 1$$

$$N \cdot \sqrt{\frac{2\pi m}{\beta}} = 1 \Rightarrow N = \frac{\sqrt{\beta}}{\sqrt{2\pi m}}$$

$$\rho(u) du = \frac{\sqrt{\beta}}{\sqrt{2\pi m}} e^{-\frac{\beta}{2} m u^2}$$

$$N = \sqrt{\frac{m}{2\pi k_B T}}$$

$$\rho(u) du = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{\beta}{2} m u^2}$$

$$a = \frac{\beta m}{2}$$

Useful integrals

$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

So, let us be careful not hurried along. So, a here is beta m over 2. So, I should have pi over a which should have been yes, I am sorry. So, let us just correct this thing. N is equal to N into the integral is 2 pi kBT divided by m this is 1. So, n is root of m transition state divided by 2 pi kBT it just shows that you can do this integral a million times and in practice even still make mistake. So, rho 1D u du finally becomes root of mTS 2 pi kBT half mu square, so just a tiny mistake of factors.

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Transition state rate

$$\text{Rate} = \int_0^{\infty} du D \rho(u) u$$

$$D = \frac{\sqrt{2\pi m^{\ddagger} k_B T} q_{\ddagger}^{\ddagger}}{h q_A^{\ddagger} q_B^{\ddagger}} e^{-E_A/k_B T} [A][B] \checkmark$$

$$\rho(u) du = \frac{\sqrt{m^{\ddagger}}}{\sqrt{2\pi k_B T}} e^{-\beta \frac{1}{2} m^{\ddagger} u^2} \checkmark$$

$$= D \int_0^{\infty} \sqrt{\frac{m^{\ddagger}}{2\pi k_B T}} e^{-\frac{\beta}{2} m^{\ddagger} u^2} u du$$

$$= D \cdot \frac{\sqrt{m^{\ddagger}}}{\sqrt{2\pi k_B T}} \int_0^{\infty} e^{-\frac{\beta}{2} m^{\ddagger} u^2} u du$$

$$= \frac{1}{2} \frac{\beta m^{\ddagger}}{\beta} = \frac{D \sqrt{k_B T}}{\sqrt{m^{\ddagger}}} \sqrt{\frac{m^{\ddagger}}{2\pi k_B T}}$$

$$= D \sqrt{\frac{k_B T}{2\pi m^{\ddagger}}}$$

$$a = \frac{\beta m^{\ddagger}}{2}$$

Useful integrals

$$\int_0^{\infty} dx x e^{-ax^2} = \frac{1}{2a}$$

But I have got this right here this is right. So, again I have got the factors here. So, I have to do this kind of an integral. So, I have some pre factors, let me just look at this integral then.

But this integral value I have also provided you here and let me be careful this time a here is beta m TS divided by 2, a is the factor behind u square.

So, I should get this integral as 1 over 2 into beta m TS divided by 2. So, this integral is nothing but kBT divided by m TS and I have the factor of D into root m TS divided by 2 pi kBT. So, I multiply by D into root m TS divided by kBT. So, this becomes equal to D into root kBT divided by m TS you see that I have this expression and the root of this expression. So, I can simplify it like this, great.

I think I have forgotten some pi I had a 2 pi kBT I am sorry, I am missing all my factors today I have a 2 pi here. So, 2 pi written here. So, let me write this very clearly D kBT over 2 pi m transitional state.

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Transition state rate

$$\text{Rate} = \int_0^{\infty} du D \rho(u) u = D \sqrt{\frac{k_B T}{2\pi m^{\ddagger S}}}$$

$$D = \frac{\sqrt{2\pi m^{\ddagger S} k_B T}}{h} \frac{q_{TS}^{\ddagger}}{q_A^{\ddagger} q_B^{\ddagger}} e^{-E_A/k_B T} [A][B]$$

$$\text{Rate} = \frac{\sqrt{2\pi m^{\ddagger S} k_B T}}{h} \frac{q_{TS}^{\ddagger}}{q_A^{\ddagger} q_B^{\ddagger}} e^{-E_A/k_B T} [A][B] \sqrt{\frac{k_B T}{2\pi m^{\ddagger S}}}$$

$$\text{Rate} = \frac{k_B T}{h} \frac{q_{TS}^{\ddagger}}{q_A^{\ddagger} q_B^{\ddagger}} e^{-E_A/k_B T} [A][B]$$

$$\text{Rate} = k [A][B]$$

$$k_{TST} = \frac{k_B T}{h} \frac{q_{TS}^{\ddagger}}{q_A^{\ddagger} q_B^{\ddagger}} e^{-E_A/k_B T}$$

Useful integrals

$$\int_0^{\infty} dx x e^{-ax^2} = \frac{1}{2a}$$

$$\text{Rate} = \int_0^{\infty} du D \rho(u) u$$

So, I have just simplified the expression from the last slide, the rate was given to me this D comes out the remaining thing I integrated in the last slide to get this, d I have calculated to be equal to this. So, I take this and multiply by a kBT over 2 pi m and when I do that, I noticed that some factors happily cancel factors are not cancel you must have to do something wrong.

So, this is equal to root kT into root kT, kBT over h, q transition state qA naught, qB naught. So, if you compare it to the expression that rate equal to phenomenological if I write k A into B, then the rate constant is equal to this is very famous expression, the transition state rate expression and now you have known the proof of this.

So, this expression is very popular. You can pick up almost any journal in physical Chemistry these days, there will be at least one article that will be using this formula. In fact, whenever a new study is started, and you have to think about rates for that reaction, whatever you are studying, this is the formula you use to make your first estimate. Of course, we have made a number of assumptions in getting here. But this is still our first estimate. And we can think about how to improve upon our assumptions later on.

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Summary – module 21

- Assumption 1: Transition state exists
- Assumption 2: Classical treatment of nuclei
- Assumption 3: No re-crossing; i.e. particles do not come back from product well
- Assumption 4: Transition state is in thermal equilibrium with the reactants
- Assumption 5: At the transition state geometry, Hamiltonian is separable

$$k_{TST} = \frac{k_B T}{h} \frac{q_{TS}^\ddagger}{q_A^0 q_B^0} e^{-E_A/k_B T}$$

So, in summary, we have made 5 assumptions in deriving transition state theory. First transition state exists without that his theory is not applicable. That is the crux, that is the basis of our theory. Secondly, think of treating nuclear classically. Third, we assumed that there is no recrossing once you go from traditional state to product, you do not come back that is actually one of the most serious assumptions and in coming models, we will think on what we can do about them, what we can do about this assumption.

Fourth is that a transition state is at thermal equilibrium. This is usually a very very good assumption. And fifth assumption is that the transition state... at the transition state geometry, I can separate the Hamiltonian along the reaction coordinate and every other coordinate under these 5 assumptions, we have shown that the transition state rate is given by this expression, where these partition functions are partition functions per unit volume. So, with that we end this module today. And in the next module, we will look at how do we calculate these, these rate constants. Thank you very much.