Chemical Kinetics and Transitional State Theory
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Lecture No. 25
TST: an intuitive proof in one dimension

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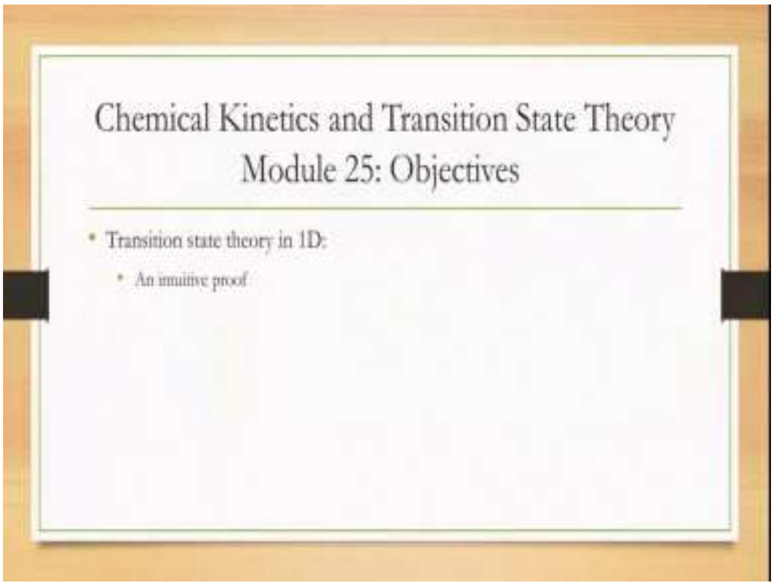

Chemical Kinetics and Transition State Theory
Module 25: Objectives

- Transition state theory in 1D:
  - An intuitive proof

Hello and welcome to module 25 of Chemical Kinetics and Transition State Theory. So, we have been playing around with transitional state theory for sometimes we looked at its derivation from statistical mechanics, we solved numerical problems and we analysed its relation with collision theory in the last module. What I want to do today and in the next module is look at the derivation from a very different perspective which is dynamical proof in phase space.

This is not usually covered in many courses or in any books. So, this proof is not there in Laidler’s book, I will provide you with appropriate reference in the next module. But today I just want to build towards its dynamical proof; I want to provide you an intuition. So, the statistical mechanisms proof is perfectly correct but it does not provide you intuition. Particularly, it does not have the intuition of dynamics in it.

It is all very static, it is all, they come from the in language of partition function and equilibrium constant and it gets to the final answer. But you know what we have studying is dynamics, we are studying kinetics, so the motion of atoms in molecules have to be present somewhere and we even show that we can derive the transition state theory result from looking at just perspective as well.

So, today let us build this intuition we will have, today we will not stick to very mathematical rigger we will be doing hand wavy proofs today in one dimension just to understand just to build an intuition. So, let us start simple.

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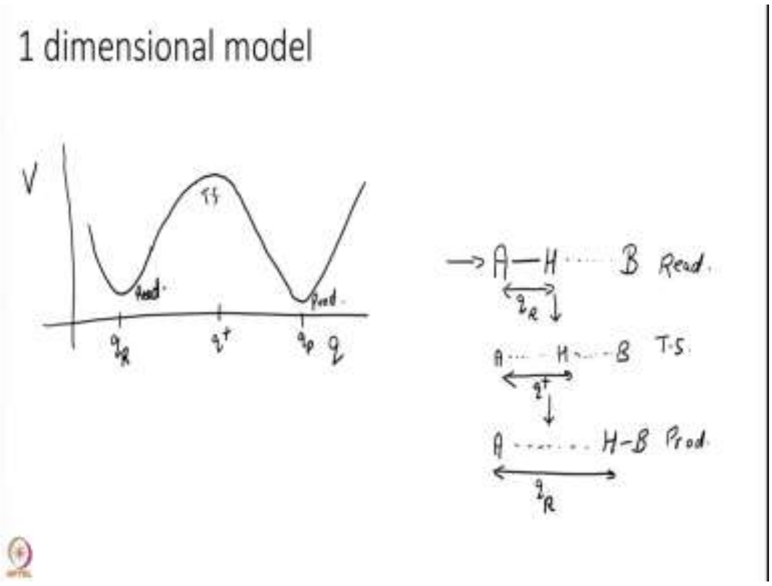
1 dimensional model

So, let us first let me build the model for you what I want to think about today. So, let us imagine some reaction I have, let us imagine I have some AH H is hydrogen and A is some hydrogen or some reactant and I have a protine expector, a hydrogen expector B. So, I have a reaction that is happening here where H let us say transfers from A to Be, this happens inside a body all the time that provide hydrogen transfer proton transfer and so all.

And let say I have some kind of a transition state in between, where H is in between neither connected to A neither connected to B but somewhere in between so this is my reactant, this is transition state and this is product. Well of course it is a complex system A and B can be some large molecules you can have solvent surrounding all of these, today I just want to keep it simple. I want to look at one dimension only which is let say this distance.

So, this distance increases here and this distance is much larger for product. And I want to think of this distance as my reaction coordinate and this is only distance that exists of the coordinates of within A or AB distance just for simplicity I will not consider today. In the next module we will think about how to include those as well.

So, if I let us you want to draw a potential energy with respect to this q, well then q is small corresponding to this one, when q corresponds to this reactant dispense you know I will have some kind of a minima which basically says that AH is forming a bond, though never you have a bond you have a minima energy surface.

But transition state distance well transition state by definition should have a maximum along the reaction coordinate I have only 1 coordinate which is a reaction coordinate and then q is very large you will have another minima. So, this is my reactants, this is the transition states, this is the product. I simply want to understand transition state theory for this simple 1 dimensional model today. So, nothing complex.

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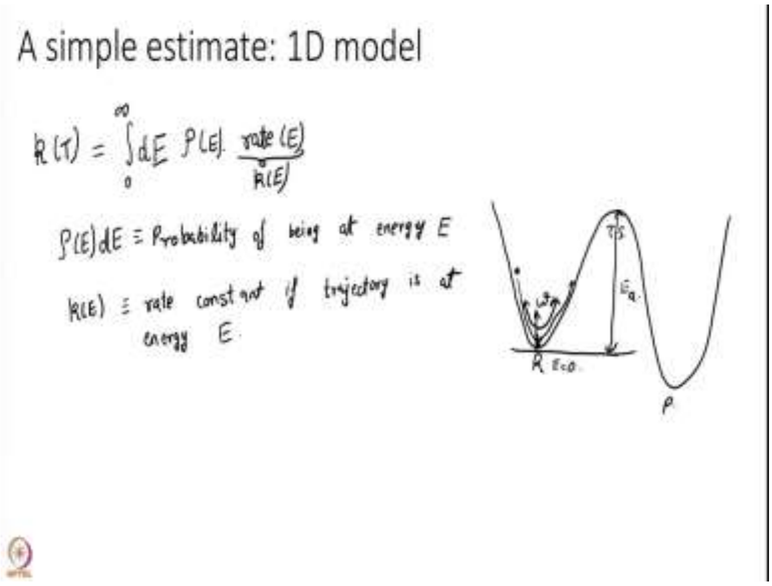

A simple estimate: 1D model

$$k(T) = \int_0^\infty dE\, \rho(E)\, \underbrace{\text{rate}(E)}_{k(E)}$$

$\rho(E)dE \equiv$ Probability of being at energy E

$k(E) \equiv$ rate constant if trajectory is at energy E.

Let me before I do transition state theory let us think of a simple minded back of the envelop estimate based on a intuition of dynamics. So, let me draw this energy surface once more. This is reactants, transition state, product. I will think that this thing at minima reactants has some frequency omega, the spring constant, omega is related to the spring constant. So, if I want to calculate the rate constant of this problem at some temperature how do I calculate it?

Well the simple thing is let us say I have a trajectory here that is moving on this, what I am going to do is think of different trajectories at different energies. So, market trajectory number 1 is at energy E1, I calculate the rate for this trajectory at even I think of another trajectory at energy E2 and I calculate that rate and I basically find a average.

More mathematically, what I am doing is, I am integrating over all possible energies I have to find the probability density of being at that energy multiplied by the rate at that energy so I will call this k of E just for that it is easier for me to write. So, what I have is rho of E dE is the probability of being at energy E and this k of E is my rate constant if trajectory is at energy E.

So, I have to calculate this rho and I have to calculate this k and I have to integrate. What should be the integration limits? It should be 0 to infinite. Energy is always positive because you always have kinetic energy which is positive and then assuming this is equal to 0 and this is Ek activation energy. So, I a integrating for all positive energies.

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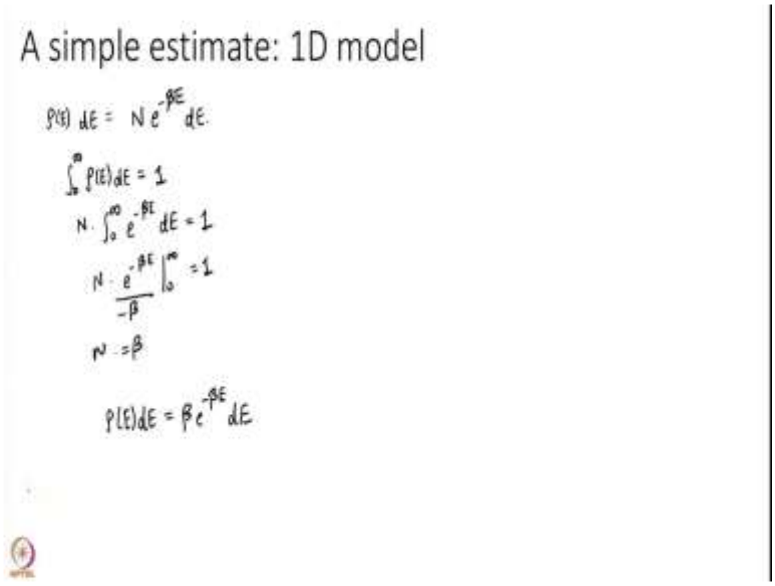

A simple estimate: 1D model

$$\rho(E)\, dE = N e^{-\beta E} dE$$

$$\int_0^\infty \rho(E) dE = 1$$

$$N \cdot \int_0^\infty e^{-\beta E} dE = 1$$

$$N \cdot \frac{e^{-\beta E}}{-\beta} \Big|_0^\infty = 1$$

$$N = \beta$$

$$\rho(E) dE = \beta e^{-\beta E} dE$$

So, let us calculate these quantities. So, we will start with this rho of E dE. Well, this is nothing but the Boltzmann division. So, rho of E dE is the my Boltzmann distribution into some normalization constant. So, the probability that I am at energy E is simply given by this, the only trick remains in calculating this N.

So, I know that my probability should be normalized. So, as I integrate the probability density from 0 to infinity I should get 1. So, N into 0 to infinity E to the power of minus beta E dE must be 1. So, N I integrate this from 0 to infinity should be 1, I solve for this I get N equal to beta. You can quickly verify this I skipped 1 or 2 sentences here.

So, I get rho of E dE equal to beta E to the power of minus beta E dE. I do not know why I have put this thing here let me remove that.

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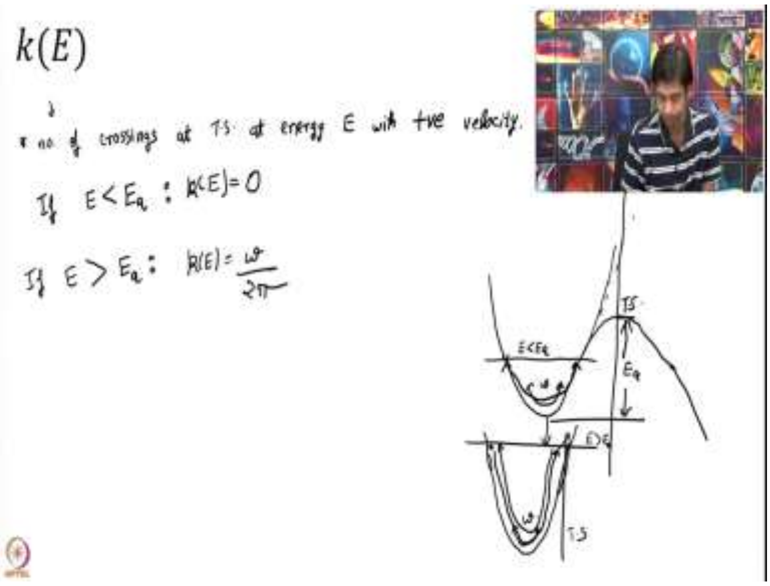

$k(E)$

↓

= no. of crossings at T.S. at energy E with +ve velocity.

If $E < E_a$: $k(E) = 0$

If $E > E_a$: $k(E) = \frac{\omega}{2\pi}$

Now, let us calculate this k of E so how do I calculate k of E that is a harder question. So, we are going to again, everything is simple minded, we are going to make simple minded we are going to make simple minded assumptions here. So, remember I transition are surface looks like this and the frequency here is omega. What I am going to do is as follows. I will imagine this to be a harmonic oscillator like this.

So, this I have converted into a harmonic oscillator with frequency omega. And what I am doing is, I am sitting at the transition state and I am asking the question at energy E what is the rate of moving forward? So, if you are at energy E what is the rate constant at which you will hit this energy surface with a positive velocity that is what is transition state theory. it only looks at positive velocity.

So, this thing is rate, so let me be more precise, a number of crossings at transition state at energy E with positive velocity, we do not include negative velocities in transition state theory that is an extremely important fact to realise and of course it is an approximation. So, how do I estimate this?

So, the first thing I realise is if E is less than Ea, if my energy is below this, well then I will not hit the reaction coordinate. I will not hit the transition state. So, if my energy is here, I will oscillate between this point and this point. I will have no possibility of reaching transition state.

So, k of E will be 0, the number of crossings at transition state is equal to 0, if E is greater than Ea, that is when I will invoke this harmonic approximation. I will think of this problem as completely this parabola, this is my transition state, so per second what is the frequency of I will hit this transition state given that I have high enough energy now? So, k of E then will be omega over 2 pi. So, omega over 2 pi is the frequency of a harmonic oscillator.

So, each point in one time period if covered twice, remember that I go from here in one time period, I do this motion and I return back, but I am looking only the crossing with positive velocity. Therefore, I ignore the negative portion and so k of E is simply omega over 2 pi. If I included the negative one as well, then I would have to double it, but those are ignored transition state. So, I have a k of E now with me.

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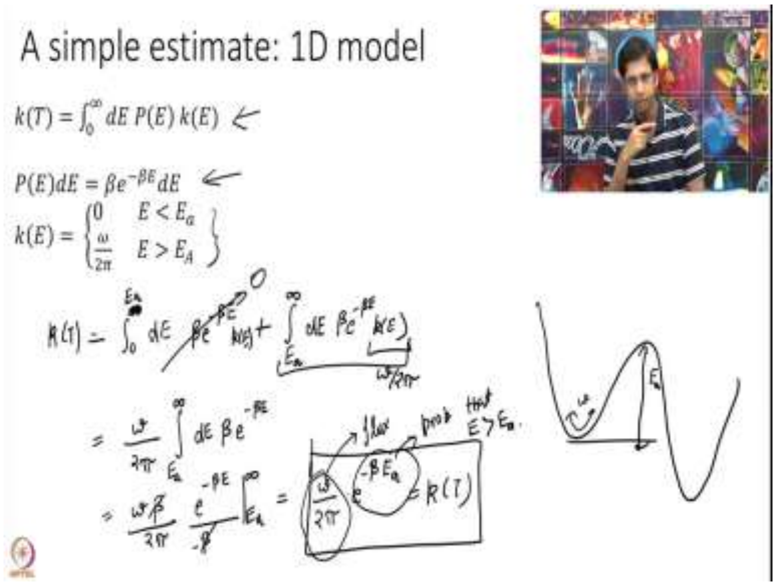

A simple estimate: 1D model

$k(T) = \int_0^\infty dE\, P(E)\, k(E) \leftarrow$

$P(E)dE = \beta e^{-\beta E} dE \leftarrow$

$$k(E) = \begin{cases} 0 & E < E_a \\ \frac{\omega}{2\pi} & E > E_A \end{cases}$$

$$k(T) = \int_0^{E_a} dE\, \overset{0}{\cancel{\beta e^{-\beta E} k(E)}} + \underbrace{\int_{E_a}^{\infty} dE\, \beta e^{-\beta E} \underbrace{k(E)}_{\omega/2\pi}}$$

$$= \frac{\omega}{2\pi} \int_{E_a}^{\infty} dE\, \beta e^{-\beta E}$$

$$= \frac{\omega \cancel{\beta}}{2\pi} \frac{e^{-\beta E}}{-\cancel{\beta}} \Bigg|_{E_a}^{\infty} = \boxed{\frac{\omega}{2\pi} e^{-\beta E_a} = k(T)}$$

flux

prob that $E > E_a$.

So, k of T we argued is given by this integral here, we argued P of E to be the thermal equilibrium P of E and k of E we have argued to be this, again a simple minded model. So, I get k of T, I just substitute things here dE, P of E is beta into e to the power of minus beta E into k of E. So, k of E will be 0, so I take this integral and take it into two parts and note that the k of E here is 0, so this is o, this portion from 0 to Em. And so I will get this 1 where k of E is simply omega over 2 pi.

So, this is an integral with omega over 2 pi that I take outside the integral Ea to infinity dE beta e to the power of minus beta E. So, this is an easy integral to do again, so let us do it. This I integrate as from Ea infinity so this will be equal to omega over 2 pi into beta will cancel with beta here and you will get is e to the power of minus beta Ea after you put in the limits. This you can easily verify. So, this is what I have got for k of T, a simple minded result.

I have a surface that looks like this, have a frequency omega here, I have activation unit. So, actually this result is very physical, omega over 2 pi is my flux, so that is the rate constant that I will traverse the reaction this transition state. This thing is probability that energy is greater than Ea for 1D only. So, I multiple by the flux with the probability that my energy is greater than Ea. It is as simple as, that is my rate constant.

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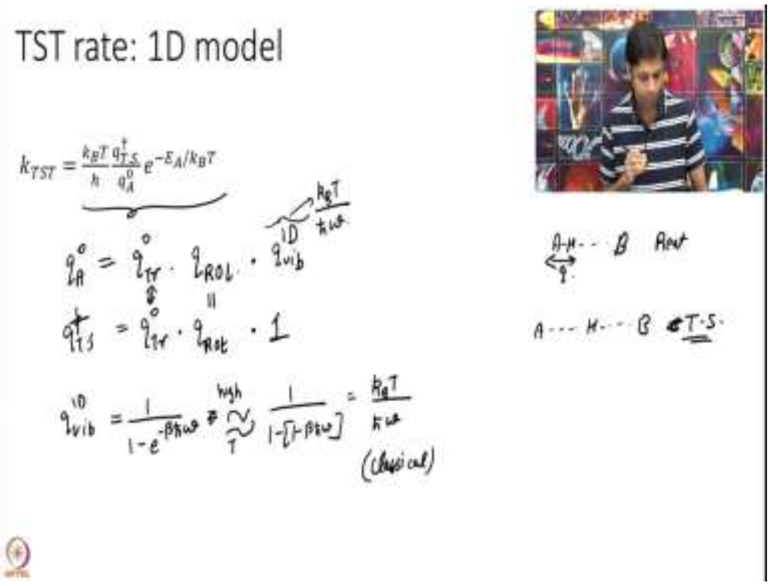

TST rate: 1D model

$$k_{TST} = \underbrace{\frac{k_BT}{h}\frac{q^{\ddagger}_{T.S.}}{q^0_A}e^{-E_A/k_BT}}$$

$$q^0_A = q^0_{Tr} \cdot q_{Rot} \cdot \overbrace{q^{1D}_{vib}}^{\frac{k_BT}{\hbar\omega}}$$

$$q^{\ddagger}_{TS} = q^0_{Tr} \cdot q_{Rot} \cdot 1$$

$$q^{1D}_{vib} = \frac{1}{1-e^{-\beta\hbar\omega}} \overset{\text{high}}{\underset{T}{\approx}} \frac{1}{1-[1-\beta\hbar\omega]} = \frac{k_BT}{\hbar\omega}$$

(classical)

A-H - - B Reat

q

A - - - H - - - B T.S.

Let us get back to transition state theory which gives you a much more sophisticated rate formula. This looks much more involved, is it at all somehow related to the formula that we have just written? We are going to think about it. Here, I have only one reactant, this A. I have my reactant is simply this one structure A-H B. So, it is governed only by this q and my transition state is once more some structure that looks like this transition state.

So, we are going to make very rough approximations for that partition functions. We have to calculate this qA naught and qTS. So, let us make rough estimate of this qA naught and qTS. qA naught, well I will have a very simple minded model, so I will not include any, only I will include only one vibration. I have some transitional, I have some rotational of the entire molecule and I will include only one vibrational, only 1D, all other vibrations and for simplicity I will ignore, just to be able to correlate with my previous simple minded answer.

qTS, I will actually the transitional part I will assume is equal, as a lead that is a very good approximation because the mass will not change in this simple minded structure. More importantly even the rotational part, we will assume is equal and the vibrational part we will assume is 1. So that 1 vibrational coordinate that was there is my reaction coordinate and so there is no vibrational component to transition state.

Remember that transition state always has 1 vibration less compared to the total number of vibrations. I am considering only here one vibration, so the total number of vibrations becomes 0. Now q vibration in 1D classically is, quantum mechanically is given by 1 minus beta h bar omega. This we can go back and see there is a, we had derived this and so we are going to make an approximation now.

We are going to assume high (tame) high temperature. So, this will become 1 minus 1 minus beta h bar omega in high temperature limit, so this is equal to kT over h bar omega which is a same as the classical answer. So, we are going to replace this by kT over h bar omega.

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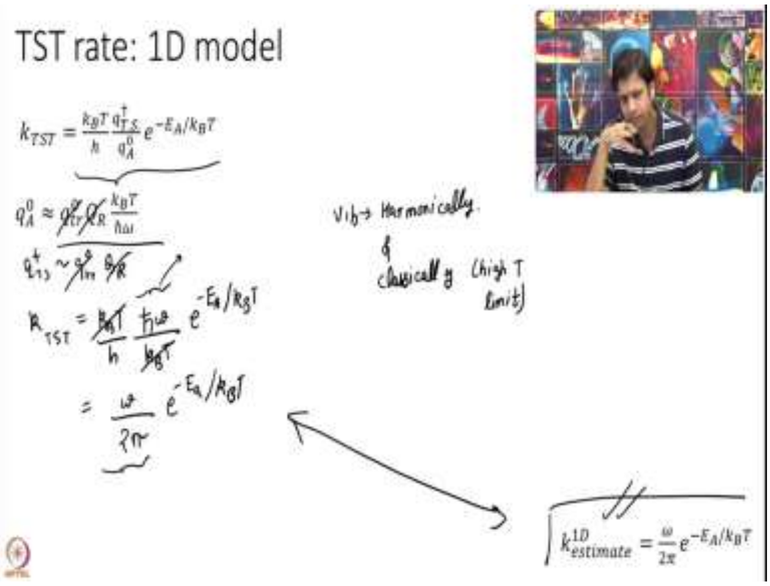

TST rate: 1D model

$$\underbrace{k_{TST} = \frac{k_BT}{h}\frac{q^{\ddagger}_{TS}}{q^0_A}e^{-E_A/k_BT}}$$

$$q^0_A \approx \cancel{q^0_{tr}}\,\cancel{q_R}\,\frac{k_BT}{\hbar\omega}$$

$$q^{\ddagger}_{TS} \sim \cancel{q^0_{tr}}\,\cancel{q_R}$$

$$k_{TST} = \frac{\cancel{k_BT}}{h}\,\frac{\hbar\omega}{\cancel{k_BT}}\,e^{-E_A/k_BT}$$

$$= \frac{\omega}{2\pi}\,e^{-E_A/k_BT}$$

Vib → Harmonically
&
classically (high T limit)

$$k^{1D}_{estimate} = \frac{\omega}{2\pi}e^{-E_A/k_BT}$$

So, I have got qA naught as some q transitional into q rotation into kT over h bar omega. q transition state is the same as qtr naught into QR. So, kTST if I divide the two, first of all I have kT over h and then if I divide the two, this will cancel and this will cancel if I am diving them and I will be left with h bar omega over kBT. So, qA naught is in the denominator, so I invert it into e to the power of minus EA over kT.

Now you notice something beautiful happens and I get h1 divide by h which is nothing but 1 over 2 pi, notice something beautiful? You get the same simple minded answer. For the idea is this thing we derived, remember how we calculated this? We assume that the rotational component is the same, we also assume one dimensional simple answer and that answer we are treating harmonically, so the vibration is treated harmonically that is a simple harmonic oscillator and classically, high temperature limit.

So, in that limit, our simple 1D estimate back of the invalid estimate basically works. And this is actually a very powerful estimate, this is your somebody with throws a reaction at you and off the top of your head you have to come up with a number on what the rate constant is going to be, this is what you do actually.

You think on what is the reaction coordinate at the transition, at the reactants, you think of what that frequency is, you estimate the activation energy somehow and you calculate this and you will get a rate constant out. It is a very simple minded, but nonetheless like it is a starting point you can say calculating this involves more calculations and it will be of course more accurate.

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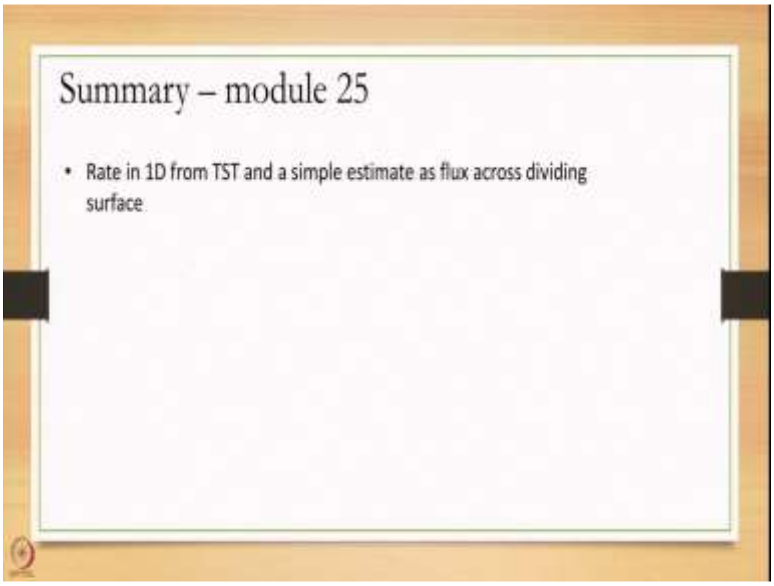

Summary – module 25

- Rate in 1D from TST and a simple estimate as flux across dividing surface

So, I want to stop here and today what we have done really is, we have calculated a 1D rate as a flux across its dividing surface, what we have done is we have put a marker on my transition state and I was looking at the flux of trajectory is moving in the positive direction at the transition state and from that we calculated the rate constant as omega over 2 pi e to the power of minus beta Ea and that we saw actually matches in some limit with the transition state answer we have already derived.

So, we will take this idea forward, in the next module we will make it much more precise. Today was hissy, today was I waved my hands, next time I want to be more accurate and put everything in correct perspective in the dynamics in phase space and derive the transition state rate again from this ides of a flux at the transition state surface. Thank you very much.