Chemical Kinetics and Transition State Theory

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Lecture 27

Transition State Theory: Derivation 2 from Dynamical Perspective

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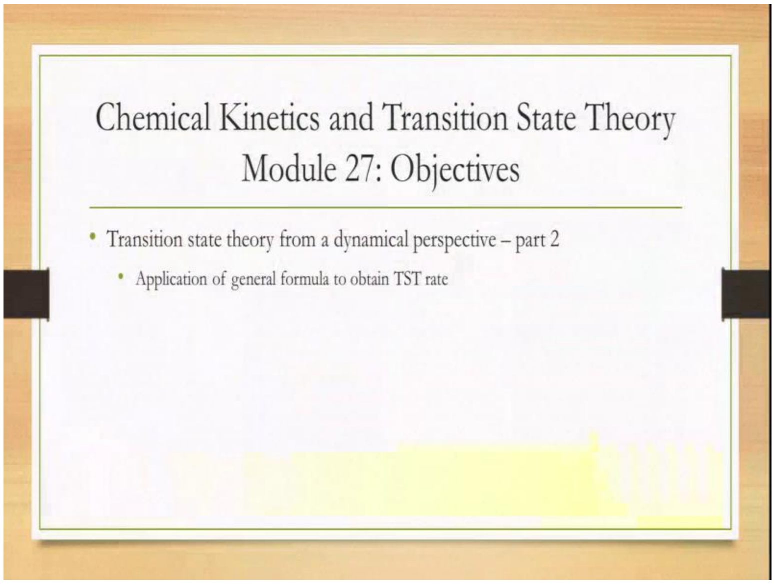

Chemical Kinetics and Transition State Theory
Module 27: Objectives

- Transition state theory from a dynamical perspective – part 2
  - Application of general formula to obtain TST rate

Hello and welcome to module 27 of Chemical Kinetics and Transition State Theory. This really is a continuation of the last module. What we discussed in the last module is a very general formula to calculate rate constants with minimal assumptions. Today, we are going to take forward that formula and make a few more assumptions to get to the transition state rate. So, again what we are doing is a different derivation of transition state theory from a dynamical perspective. Earlier we had derived it from statistical mechanics, now we are deriving it from direct dynamics as flux across a dividing surface or the number of trajectories passing per second across a surface that divides reactants and products that is what our rate is.

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Resources

- Chemical kinetics and dynamics, Steinfeld, Francisco and Hase, Chapter 10
- Bruce Mahan, J. Chem. Ed. **51,** 709 (1974): https://pubs.acs.org/doi/pdf/10.1021/ed051p709

Again, the work I am following, you can either find in Steinfeld, Francisco and Hane, Chapter 10 or this excellent paper by Bruce Mahan in Journal Chemical of Education, you can also find the same arguments there.

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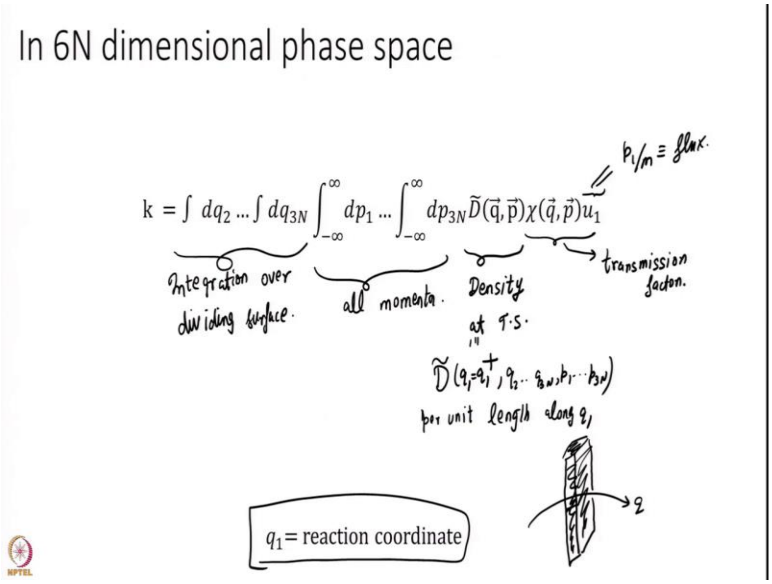

In 6N dimensional phase space

$$k = \underbrace{\int dq_2 \ldots \int dq_{3N}}_{\text{Integration over dividing surface.}} \underbrace{\int_{-\infty}^{\infty} dp_1 \ldots \int_{-\infty}^{\infty} dp_{3N}}_{\text{all momenta.}} \underbrace{\tilde{D}(\vec{q},\vec{p})}_{\text{Density at T.S.}} \underbrace{\chi(\vec{q},\vec{p})}_{\text{transmission factor.}} \overset{p_1/m \equiv \text{flux.}}{\widetilde{u_1}}$$

$$\tilde{D}(q_1 = q_1^{\dagger}, q_2 \ldots q_{3N}, p_1 \ldots p_{3N})$$

per unit length along q_1

$\boxed{q_1 = \text{reaction coordinate}}$

So, in the last module, we ended with this particular formula for rate constant. We had integrated over all coordinates that is not the reaction coordinate. So, we have one coordinate that we call the reaction coordinate. So, this is an integration over dividing surface. So, I am sitting at a transition state, one coordinate is my reaction coordinate. Every other direction is perpendicular to this and constitutes my dividing surface.

So, I am integrating over all this dividing surface. This is, here is reactant, here is product and this is the surface in between. I am integrating over all momenta. D here, tells me density at transition state. So, I have used a little bit of short hand notation, what this is, is exactly q1 equal to q1 dagger, that is q1 is set at the transition state and all other coordinates. So, this is my density per unit length along q1.

So, I have my q1 here. This is my dividing surface here. So, I am looking at the density in this direction, how many particles will fall into this little region. Chi is what we defined as transmission factor. That is, if I am at a transition state at some point with some speeds or momentum, what is the probability that that point originated from the reactant and will end up in the product.

So, we are only interested in the forward reaction of going from reactant to product. And this chi tells me that this coordinate point, q comma p, is it coming from the reactant in the past and will it end up in the product in the future. And finally, this u1 equal to p1 over m is nothing but the flux, that is a technical language we use. But that basically tells me how many trajectories per second will go through.

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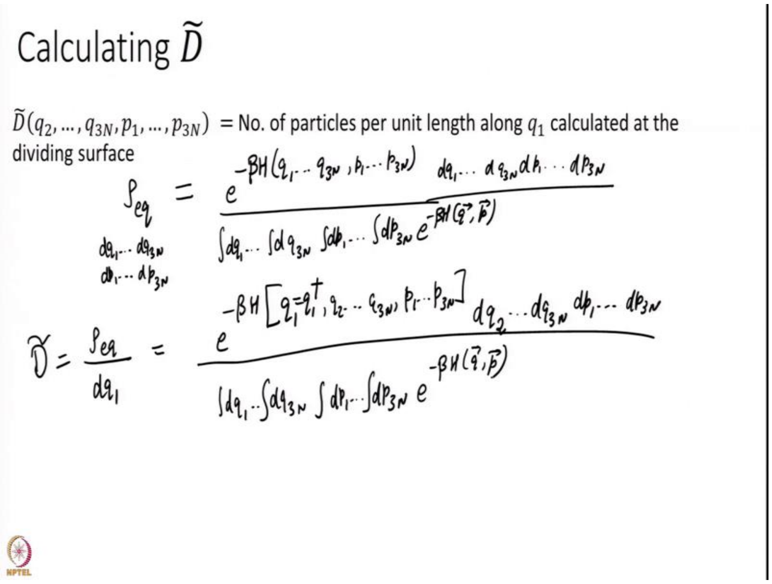

Calculating $\widetilde{D}$

$\widetilde{D}(q_2, \ldots, q_{3N}, p_1, \ldots, p_{3N})$ = No. of particles per unit length along q_1 calculated at the dividing surface

$$\rho_{eq}\,{}_{dq_1 \cdots dq_{3N}\, dp_1 \cdots dp_{3N}} = \frac{e^{-\beta H(q_1 \cdots q_{3N}, p_1 \cdots p_{3N})}\, dq_1 \cdots dq_{3N}\, dp_1 \cdots dp_{3N}}{\int dq_1 \cdots \int dq_{3N} \int dp_1 \cdots \int dp_{3N}\, e^{-\beta H(\vec{q}, \vec{p})}}$$

$$\widetilde{D} = \frac{\rho_{eq}}{dq_1} = \frac{e^{-\beta H[q_1 = q_1^{\dagger}, q_2 \cdots q_{3N}, p_1 \cdots p_{3N}]}\, dq_2 \cdots dq_{3N}\, dp_1 \cdots dp_{3N}}{\int dq_1 \cdots \int dq_{3N} \int dp_1 \cdots \int dp_{3N}\, e^{-\beta H(\vec{q}, \vec{p})}}$$

So now, let us think of calculating this D tilde. So, this again is the number of particles per unit length along q1. So now is when we will start making a little bit more assumptions, here we are going to assume we have thermal equilibrium. So, at thermal equilibrium, we have seen the equilibrium density. Equilibrium density is given by, at any given point, this big integral over 6N dimensions. Now, I have to find the number of particles per unit length along q1 only.

So, let us be more clear what I mean, I should have dq1 to dq3N into dp1 into dp3N, that is really the probability density. I should always have these infinite symbols with me. So, the number of particles per unit length along q1 is nothing but rho eq over dq1. So, this is what D tilde really is, if I am looking at the direction of q1 and finding the number of particles per unit length.

So, I have to divide by dq1, so I eventually get and I set q1 equal to q1 dagger. So again, I am calculating this D tilde at the transition state and the transition state is specified when q1 is equal to q1 dagger, when the reaction coordinate corresponds to the transition state geometry, Q3N, p1 to p3N, dq1 disappears and I get dq2 to dq3N, dp1 to dp3N divided by this big integral, e to the power of minus beta H q comma p. We have made some progress, we have a sense of what D tilde is.

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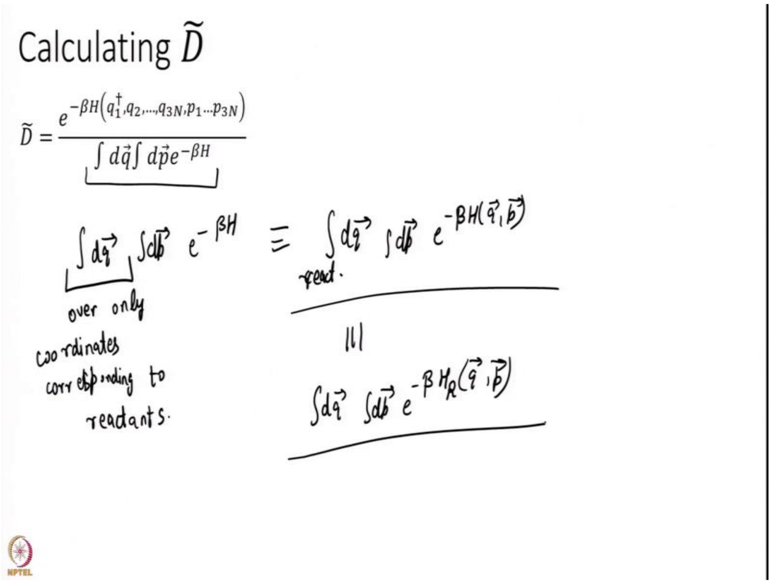

Calculating $\widetilde{D}$

$$\widetilde{D} = \frac{e^{-\beta H\left(q_1^{\dagger}, q_2, \ldots, q_{3N}, p_1 \ldots p_{3N}\right)}}{\underbrace{\int d\vec{q} \int d\vec{p}\, e^{-\beta H}}}$$

$$\underbrace{\int d\vec{q}}_{\text{over only coordinates corresponding to reactants.}} \int d\vec{p}\; e^{-\beta H} \equiv \int_{\text{react.}} d\vec{q} \int d\vec{p}\; e^{-\beta H(\vec{q},\vec{p})}$$

$$\equiv \int d\vec{q} \int d\vec{p}\; e^{-\beta H_R(\vec{q},\vec{p})}$$

Let us just look at this denominator for a moment. One important thing that I want to bring about this denominator is that this does not integrates over all coordinates. This is a hard concept to understand. Remember what we are doing, we are looking only for transitions that occur from reactant to product. To do that, we basically get rid of all population on the product side. We only have population in our reactants and we are looking at how many trajectories are becoming products. So, this integral that we have we integrate over only coordinates corresponding to reactants. That is very important to understand that this integration is not over all possible coordinates. All possible coordinates will include both reactant and product.

So, we integrate over reactant configurations only, because we are interested only in one sided flux. We are looking only from reactant to product forward rate only. To calculate forward rate, I do not want anything to be there in the product side. I want the entire thing to be normalized in the reactant side only. What I am going to do is write this thing as e to the power of minus beta HR, just a notation. So, this thing is exactly the same as this thing, just a notation, just a short hand way of writing things.

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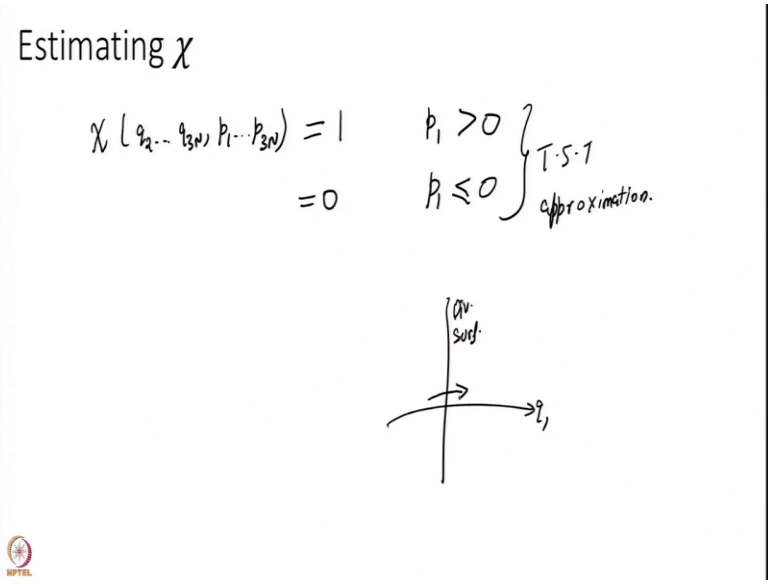

Estimating χ

$$\chi(q_2 \ldots q_{3N}, p_1 \ldots p_{3N}) = 1 \qquad p_1 > 0$$
$$= 0 \qquad p_1 \leq 0$$

T.S.T approximation.

So, the next question I have to answer is, how do I estimate this chi? Actually, that is a very hard question. We are going to make a very simple assumption and this hopefully will help you clarify what transition state theory really is. We assume chi is a big factor which depends on q2 to q3N, p1 to p3N, this is 1 if p1 is greater than 0, this is equal to 0 if p1 is less than 0. Let us make is equal as well to be more general.

So, this is the transition state theory approximation, one of the central approximations that is made in transition state theory. That is, if p1 is positive, p1 again is the momentum along the reaction coordinate. So, this is my q1, this is my dividing surface. If I have a momentum in the positive direction, then I am reactive, then I must have come from reactant in the past and I will end up in the product in the future independent of whatever this q2, q3, q3N is or whatever this p2, p3, p3N is. I do not even care about what their values are. I only look at p1, I see if p1 is positive you are traveling forward then you will end up in the product. If p1 is not less than 0, you are coming in the opposite direction, you are not allowed. So that is the essence of transition state theory.

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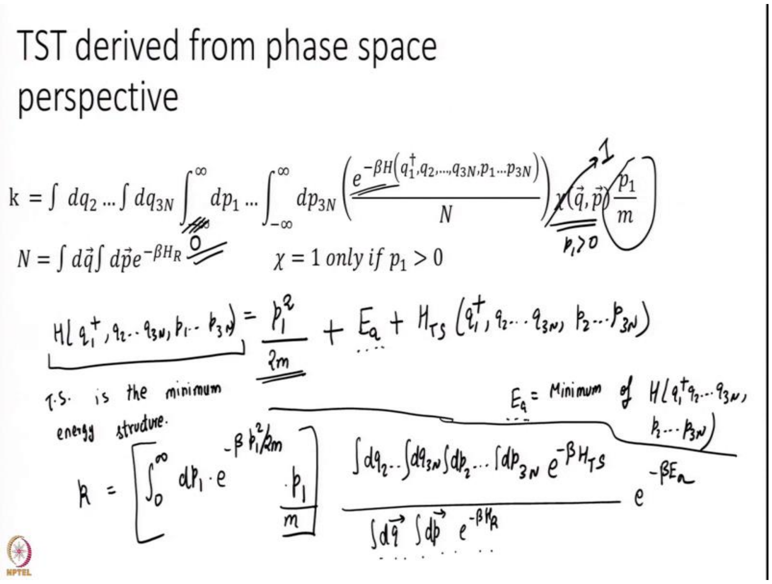

TST derived from phase space perspective

$$k = \int dq_2 \ldots \int dq_{3N} \int_{\cancel{-\infty}\ 0}^{\infty} dp_1 \ldots \int_{-\infty}^{\infty} dp_{3N} \left(\frac{e^{-\beta H(q_1^{\dagger}, q_2, \ldots, q_{3N}, p_1 \ldots p_{3N})}}{N} \right) \underbrace{\cancel{\chi(\vec{q}, \vec{p})}}_{p_1 > 0} \xrightarrow{} 1 \ \frac{p_1}{m}$$

$$N = \int d\vec{q} \int d\vec{p}\, e^{-\beta H_R}$$

$$\chi = 1 \; only \; if \; p_1 > 0$$

$$\underbrace{H(q_1^{\dagger}, q_2 \ldots q_{3N}, p_1 \ldots p_{3N})}_{\text{T.S. is the minimum energy structure.}} = \frac{p_1^2}{2m} + E_a + H_{TS}(q_1^{\dagger}, q_2 \ldots q_{3N}, p_2 \ldots p_{3N})$$

E_a = Minimum of $H(q_1^{\dagger} q_2 \ldots q_{3N}, p_2 \ldots p_{3N})$

$$k = \left[\int_0^{\infty} dp_1 \cdot e^{-\beta p_1^2/2m} \cdot \frac{p_1}{m} \right] \frac{\int dq_2 \ldots \int dq_{3N} \int dp_2 \ldots \int dp_{3N}\, e^{-\beta H_{TS}}}{\int d\vec{q} \int d\vec{p}\, e^{-\beta H_R}} e^{-\beta E_a}$$

So, we have our formulas for D and chi and all that is needed is to put into this big integral. So, let us see where that goes. So, this chi, here will be 1 only if p1 is greater than 0, otherwise it will be 0. So, I changed the integral over p1 from 0 to infinity. Because if p1 is less than 0, chi will be equal to 0 and that will not contribute at all to the integral and then I can get rid of chi to be 1. If p1 is greater than 0 then chi is 1.

Now, what I will do is, I will look at this H and simplify. I will assume the separability of the momentum of the reaction coordinate, I am separating up just the momentum of the reaction coordinate only. I will also take out the constant energy Ea, I will just specify what Ea is, please give me a moment, of q1 dagger, q2 to q3N, p2 to p3N. So, I have taken the momentum one out only. Ea is essentially the minimum of H, of this. So that is your activation energy really, because transition state structure is the minimum structure along all directions perpendicular to the reaction coordinate.

So, if I look at this H, where q1 is fixed at a transition state geometry and I am varying all their geometries, then transition state is the minimum, not maximum. This is a very common confusion. This is the minimum energy structure on this H. So, Ea is the energy of this transition state and that is your activation energy. Ea is the energy of the transition state.

So, if I do that, this k, what I will do is just separate out the p1 term, e to the power of minus beta p1 square over 2m into p1. So, I have taken this integral from e to the power of minus beta H, I have taken this term out. And this p1 over m, I have separated out. And I leave everything else as it was. So that will be integral of dq2 to dq3N, dp2 to dp3N, e to the power of minus beta H TS with all the coordinates which I am not writing for simplicity divided by the N and N is integral over all coordinates corresponding to reactants only dp, e to the power of minus beta HR.

So, this integral basically means integrating over all coordinates corresponding to reactants and I should not forget e to the power of minus beta Ea. So Ea is a number. It is not dependent on any coordinates and so, I take that outside the integral.

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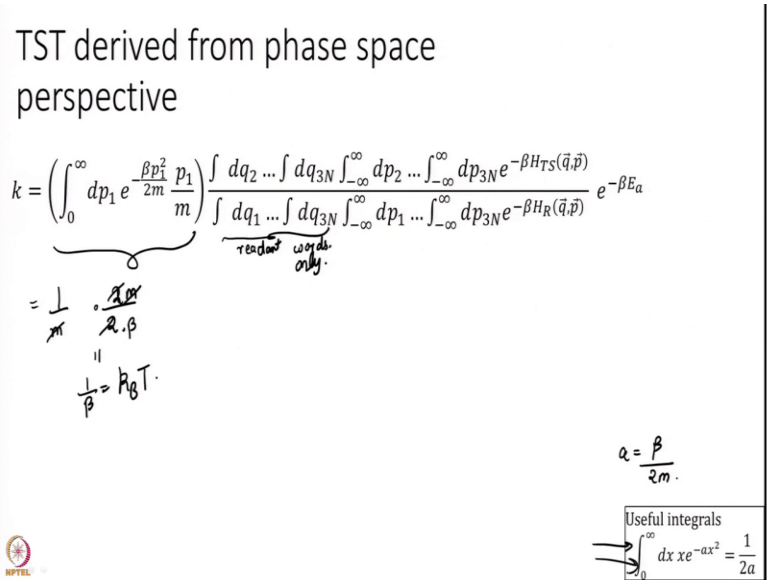

TST derived from phase space perspective

$$k = \underbrace{\left(\int_0^\infty dp_1\, e^{-\frac{\beta p_1^2}{2m}}\, \frac{p_1}{m}\right)} \frac{\int dq_2 \ldots \int dq_{3N} \int_{-\infty}^{\infty} dp_2 \ldots \int_{-\infty}^{\infty} dp_{3N} e^{-\beta H_{TS}(\vec{q},\vec{p})}}{\underbrace{\int dq_1 \ldots \int dq_{3N}}_{\text{reactant words only.}} \int_{-\infty}^{\infty} dp_1 \ldots \int_{-\infty}^{\infty} dp_{3N} e^{-\beta H_R(\vec{q},\vec{p})}}\, e^{-\beta E_a}$$

$$= \frac{1}{\cancel{m}} \cdot \frac{\cancel{2}\cancel{m}}{\cancel{2}\cdot\beta}$$

$$\|$$

$$\frac{1}{\beta} = k_B T.$$

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

Useful integrals

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

So, I arrived with this big formula. I have written it out explicitly. And once more in the denominator here, in this integration, this corresponds to reactant coordinates only. So, this is an integral that I can actually do. This formula I have provided you here. I will look at this formula. I will think of a as beta over 2m. So, this will be 1 over m, that I will take constant out into 1 over 2a, 1 over 2 into a, a is beta over 2m, 2, 2 cancels, m, m cancels. So, this integral is equal to 1 over beta which is nothing but KBT. So that is an easy integral for you to do given that this formula is provided. So, I substitute that integration as KBT.

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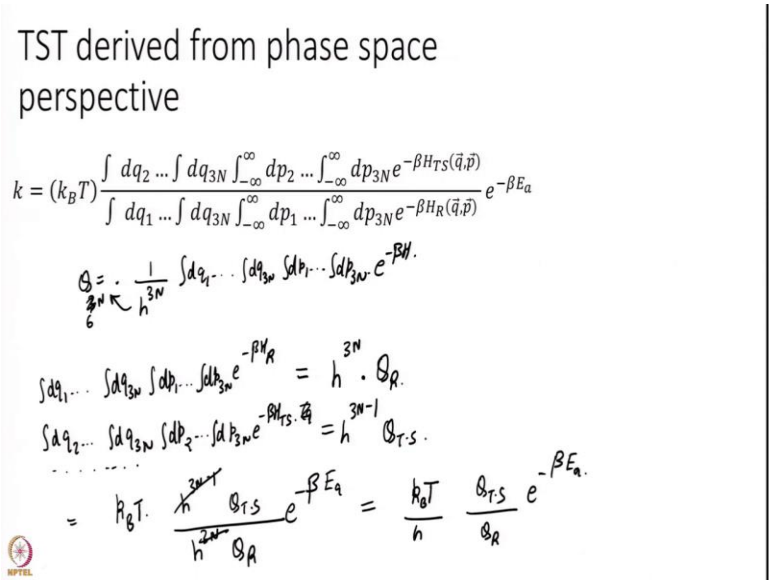

TST derived from phase space perspective

$$k = (k_B T)\frac{\int dq_2 \ldots \int dq_{3N} \int_{-\infty}^{\infty} dp_2 \ldots \int_{-\infty}^{\infty} dp_{3N} e^{-\beta H_{TS}(\vec{q},\vec{p})}}{\int dq_1 \ldots \int dq_{3N} \int_{-\infty}^{\infty} dp_1 \ldots \int_{-\infty}^{\infty} dp_{3N} e^{-\beta H_R(\vec{q},\vec{p})}} e^{-\beta E_a}$$

$$Q = \frac{1}{h^{3N}} \int dq_1 \cdots \int dq_{3N} \int dp_1 \cdots \int dp_{3N} \, e^{-\beta H}.$$

$$\cancel{3}N \quad 6$$

$$\int dq_1 \cdots \int dq_{3N} \int dp_1 \cdots \int dp_{3N} \, e^{-\beta H_R} = h^{3N} \cdot Q_R.$$

$$\int dq_2 \cdots \int dq_{3N} \int dp_2 \cdots \int dp_{3N} \, e^{-\beta H_{TS}} = h^{3N-1} \, Q_{T \cdot S}.$$

$$= k_B T \cdot \frac{\cancel{h^{3N-1}} \, Q_{T \cdot S}}{h^{\cancel{3N}} \, Q_R} e^{-\beta E_a} = \frac{k_B T}{h} \frac{Q_{T \cdot S}}{Q_R} e^{-\beta E_a}.$$

Now, we realize that the partition functions really look like these integrals. So, the partition function in 3N dimension is really defined as h to the power of 3N, 6N, sorry, dq1 to dq3N, dp1 to dp3N into e to the power of minus beta H. So, if I look at the denominator, e to the power of minus beta HR, this is nothing but h to the power of 3N into q reactants. Q reactant really by definition is the partition function of reactants only. So, I am integrating only over the coordinate of the reactants and this h to the power of 3N I have taken here.

Similarly, the numerator is h of the transition state, h into 3N minus 1. Note that one integration is less here. I have 3N minus 1 coordinates only. So once more, transition state partition function is one dimension less compared to the reactants into Q of transition state. So, if I put it here, I will get h to the power of 3N minus 1, Q transition state, divided by h to the power of 3N Q reactants, but you, I cancel lot of h, so I get KT over h Q transition state over Q reactants.

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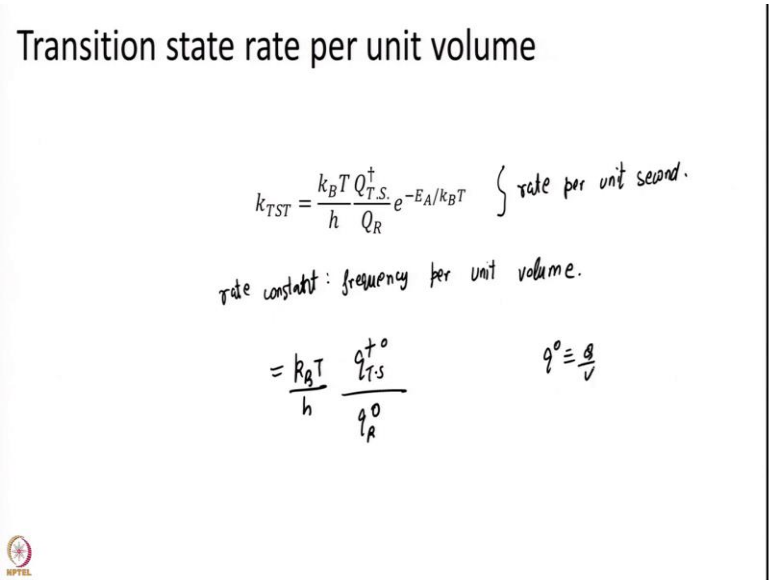

Transition state rate per unit volume

$$k_{TST} = \frac{k_B T}{h}\frac{Q^{\dagger}_{T.S.}}{Q_R} e^{-E_A/k_B T} \quad \Big\} \text{ rate per unit second.}$$

rate constant : frequency per unit volume.

$$= \frac{k_B T}{h} \frac{q^{\dagger o}_{T \cdot S}}{q^{o}_{R}} \qquad q^{o} \equiv \frac{Q}{V}$$

One final thing we have to be careful about, this formula really looks very close to what we have derived earlier from statistical mechanics. One tiny detail that is missing, what we have derived is rate per unit second. So, I am sitting at a dividing surface and simply counting the number of particles that went through in one second. But that is not what exactly rate constant is.

Remember, rate constant is the number of particle passings through per unit volume. So, the rate constant is frequency per unit volume. But that actually has a easy remedy. All we do is find the partition functions per unit volume, where my q naught is Q over V. So, I find the reactant partition functions per unit volume, I find the transition state partition functions per unit volume. That is all that I have to do then to get to the rate constant per unit volume.

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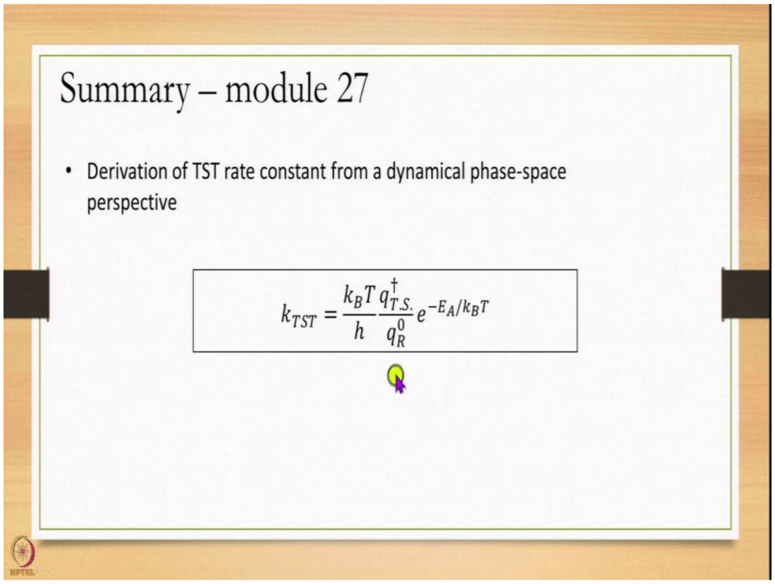

Summary – module 27

- Derivation of TST rate constant from a dynamical phase-space perspective

$$\boxed{k_{TST} = \frac{k_B T}{h} \frac{q^{\dagger}_{T.S.}}{q^0_R} e^{-E_A/k_B T}}$$

So, we end up getting the very famous formula that we had derived earlier. We get KT over h into q transition state divided by qR naught. We have been writing it for bimolecular where it becomes qA naught into qA naught, but to be honest, it always has been qR naught. We just have been looking reactants as A plus B into the Arrhenius exponential. But now we have this derivation from a very different perspectives.

Now, we have a much more intuitive way of deriving this which is that I have a dividing surface. This dividing surface separates a reactant from the products. Look at all possible positions on this dividing surface and look at the positive flux across this dividing surface that is really what all rate is, the number of particles passing per unit second, per unit volume across this dividing surface. Thank you very much.