Chemical Kinetics and Transitional State Theory

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Lecture No. 24

Collision theory as a special case of TST

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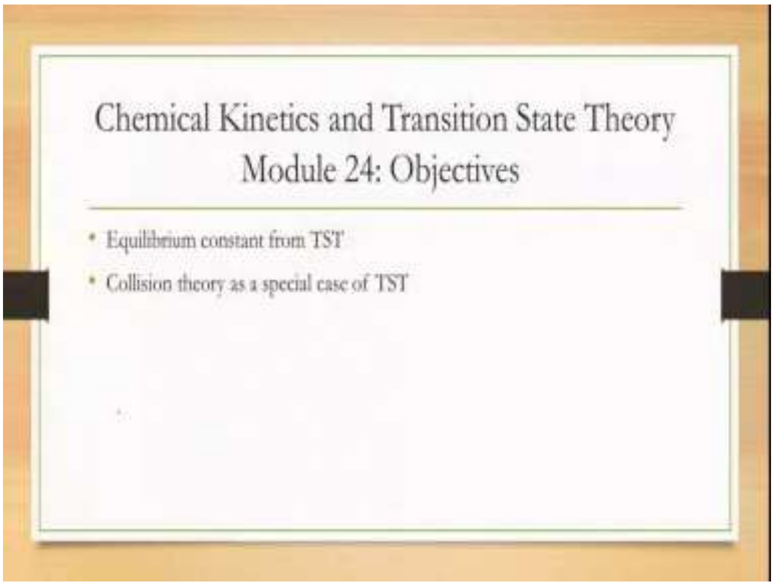

Chemical Kinetics and Transition State Theory
Module 24: Objectives

- Equilibrium constant from TST
- Collision theory as a special case of TST

Hallo and welcome to module 24 of Chemical Kinetics and Transitional State Theory. Today, we are going to cover a few basic properties of transition state theory. We have calculated the rate constant for transition state theory and we have even looked at numerical examples. So, today we will just play around with this rate and discover some interesting properties. So, let us start with one first property.

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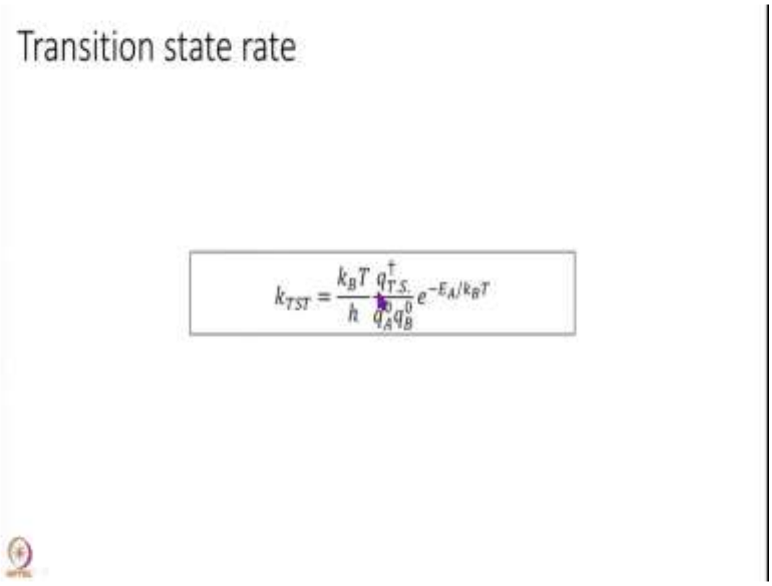

Transition state rate

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

So, this is the rate constant that we have derived from transitional state theory.

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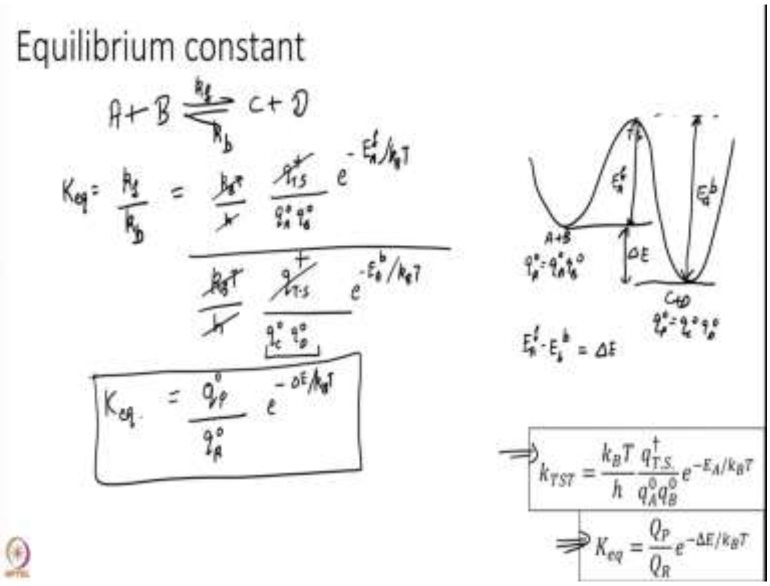

Equilibrium constant

$$A + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C + D$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{\frac{\cancel{k_B T}}{\cancel{h}} \frac{\cancel{q^{\dagger}_{T.S}}}{q_A^0 q_B^0} e^{-E_A^f/k_B T}}{\frac{\cancel{k_B T}}{\cancel{h}} \frac{\cancel{q^{\dagger}_{T.S}}}{q_C^0 q_D^0} e^{-E_a^b/k_B T}}$$

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

$E_a^f - E_a^b = \Delta E$

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

$$\Rightarrow K_{eq} = \frac{Q_P}{Q_R} e^{-\Delta E/k_B T}$$

So, let us start with the first point which is the equilibrium constant. so, transitional state theory is given here, let us assume I have some reaction that is like this, it is reversible and K equilibrium is kf over kb. So, I can calculate kf and kb both from transition state theory and take the division. So, kf will be equal to kBT over h q of transition state over q a naught q b naught e to the power of minus Ea forward over kT.

So, and I am defining a 1D surface A plus B here, C plus D here and a transition state here. So, this is Ea forward and I will also need this one, so let me define it right away Ea backward. So, this is kf divided by kBT over h. Note that the transition state is the same for both, where the same q TS rather qc naught qd naught e to the power of minus Ea b over kBT. So, you note that a lot of terms will cancel, kT over h cancels, q TS cancels and what I am left with is what I will do is write qc into qd as q products divided by q reactants.

So, q reactants naught is qa naught into qb naught and q product naught is qc naught qd naught into e to the power of minus, what I will have is EA f minus EA back, but this is what is the exothermicity of the problem. So, EA f minus EA b is simply delta E. So, I get this for k equilibrium according to transition state theory.

But this is exactly what you expect based on thermodynamics. So, this relation I derived in a few modules ago, we were discussing statistical mechanics. So, we can go back to it. And so this relation is exactly right, it matches thermodynamics perfectly. So, that is very good news, we have actually made a tremendous progress based on collision theory at least. If you go back to your collision theory, we got wrong equilibrium constant. In transition state theory, we get the correct equilibrium constant.

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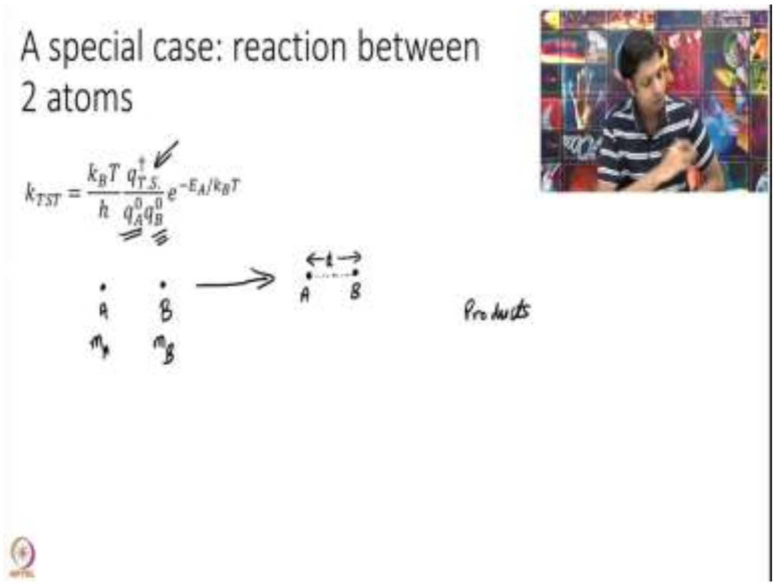

A special case: reaction between 2 atoms

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

The second thing I want to just discuss today rather interesting connection between transition state theory and collision theory. Let us just apply transition state theory to a special problem where the reactants are both atoms. So, I have A one atom, B another atom they go to some reaction, some products, I do not even care what the product is, but the transition state let us assume is simply a linear structure that looks like this. It does not actually have to be, but that is a natural thing to imagine with some distance d.

So, A and B are basically I am imagining coming close and the transition state is that A and B come close at some critical distance d which is the transition state. So, this is not really a bond by the way because transition state is a maximum energy structure along the reaction coordinate. So, I want to calculate the transition state rate for this problem. So, let us assume that A has some mass A, this has some mass B.

So, what all do I need to calculate, well I need to calculate, qa naught qb naught and q transition state. So, let us do this.

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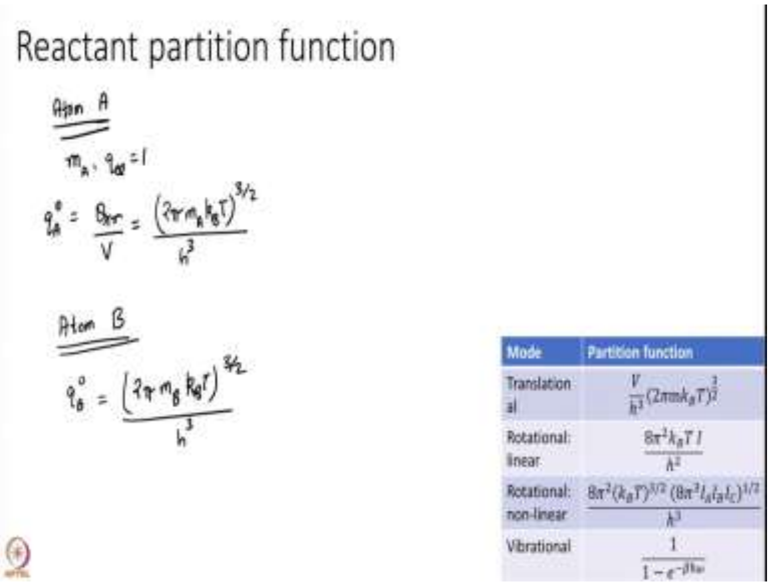

Reactant partition function

Atom A

$m_A, q_{el} = 1$

$$q_A^0 = \frac{q_{tr}}{V} = \frac{(2\pi m_A k_B T)^{3/2}}{h^3}$$

Atom B

$$q_B^0 = \frac{(2\pi m_B k_B T)^{3/2}}{h^3}$$

Mode	Partition function
Translational	$\frac{V}{h^3}(2\pi m k_B T)^{\frac{3}{2}}$
Rotational: linear	$\frac{8\pi^2 k_B T I}{h^2}$
Rotational: non-linear	$\frac{8\pi^2 (k_B T)^{3/2} (8\pi^3 I_A I_B I_C)^{1/2}}{h^3}$
Vibrational	$\frac{1}{1-e^{-\beta\hbar\omega}}$

So, my reactants are atoms A and atom B. So, here is a question for you first, what all information do you need to gather to calculate partition function of atom A? Take a little pause, think about it and then we will discuss it together. Hope that you have thought about it. It is an atom, atom has only transitional partition function and electronic partition function and atom cannot rotate and atom cannot rival it.

For rotation you need at least two atoms, same for vibration. So, rotation or vibration is between nuclei, never between a nuclei and the electron, we do not consider electrons here. So, I just need the mass of A and the electronic degeneracy. What we are doing is a rather simple analysis together, so would are assume, going to assume that all the electronic degeneracy is simply 1.

We are simply going to ignore it for simplicity, what we are doing is a simple minded analysis. So, my qA naught is simply a transitional partition function divided by volume which is nothing but a 2 pi mA kBT to the power of 3 half divided by h cube. I can do the same analysis for atom B. So, qB naught correspondingly will be 2 pi mB instead of mA everything else remains the same divided by h cube.

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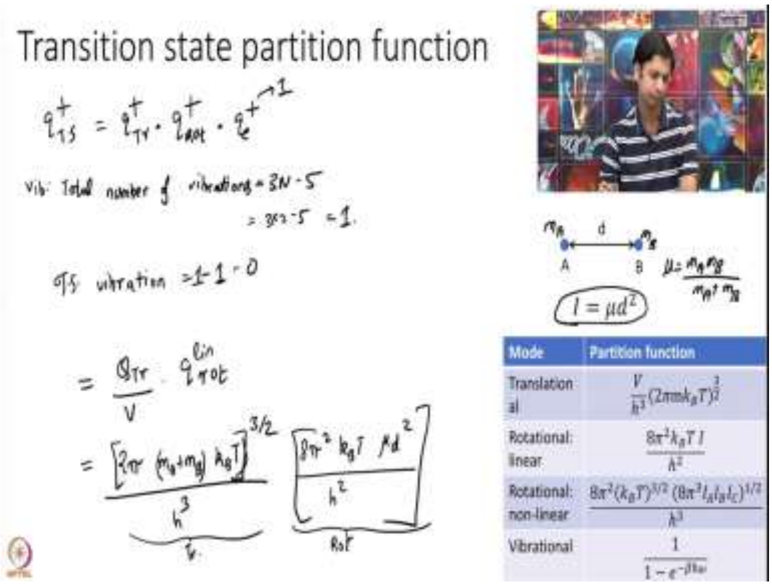

Transition state partition function

$$q^{\ddagger}_{TS} = q^{\ddagger}_{Tr} \cdot q^{\ddagger}_{Rot} \cdot q^{\ddagger}_{e}\xrightarrow{} 1$$

Vib: Total number of vibrations = 3N - 5

= 3×2 - 5 = 1.

T.S. vibration = 1 - 1 = 0

$$= \frac{Q_{Tr}}{V} \cdot q^{lin}_{rot}$$

$$= \underbrace{\frac{\left[2\pi (m_A+m_B) k_B T\right]^{3/2}}{h^3}}_{Tr} \underbrace{\left[\frac{8\pi^2 k_B T \mu d^2}{h^2}\right]}_{Rot}$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

$$\boxed{I = \mu d^2}$$

Mode	Partition function
Translational	$\frac{V}{h^3}(2\pi m k_B T)^{\frac{3}{2}}$
Rotational: linear	$\frac{8\pi^2 k_B T I}{h^2}$
Rotational: non-linear	$\frac{8\pi^2 (k_B T)^{3/2} (8\pi^3 I_A I_B I_C)^{1/2}}{h^3}$
Vibrational	$\frac{1}{1 - e^{-\beta h\nu}}$

So, let us now think of the transition state. So, transition state I am assuming to be diatomic, it well, it has to be diatomic, it cannot be anything more, but I am assuming of this particular form where your distance is d, so in that case one information I can tell you from mechanics, this can be calculated exactly, the moment of inertia for this diatomic molecule is equal to mu d square. So, once no rate is a diatomic and diatomic is by definition linear, there is no way two atoms can be non-linear.

So, the q of a transition state will be the (trans) the transitional part, it will be the rotational part, what about vibrations, will it have a vibration? Think about it once more. It will not have a vibration, why? I have two atoms, two atoms linear. So, total number of vibrations for a linear molecule equal to 3N minus 5, we have discussed it a few times, so 3 into 2 minus 5, this is 1. Well, I have 1 vibration, so what is going wrong?

Transition state requires 1 less vibration than the total number of vibrations, here transition state vibrations that I have to include in my partition function is 1 minus 1 because the 1 vibration goes into the imaginary mode which is included in kT over h of transition state rate. So, go back to your proof if you do not understand this, this is an important point, for transition state we take 1 frequency less compared to the total number of frequencies.

So, there is no vibrational part and the electronic part we are going to assume again to be 1. So, q transitional is Q transitional divided by volume into q rotational and this is of course for linear. So, I can quickly write this answer, this is 2 pi, now what is the total mass of a transition state? mA plus mB, the total A has mA, B is mB, the total is mA plus mB, kBT to the power of 3 half divided by h cube and this thing is 8 pi square, I is mu d square, this is rotational, this is transitional.

One thing I have just forgot to mention, mu is the reduced mass that we have used before, so mu is given by mA mB divided by mA plus mB. So, again this moment of inertia is actually very easy to derive, but I am not doing it here, I am simply stating it.

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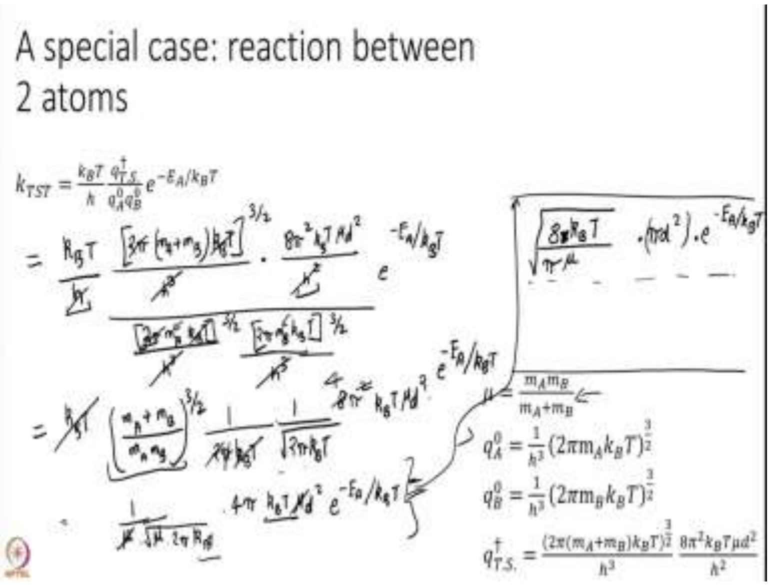

A special case: reaction between 2 atoms

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

$$= \frac{k_BT}{\cancel{h}} \frac{\frac{[2\pi(m_A+m_B)k_BT]^{3/2}}{\cancel{h^3}} \cdot \frac{8\pi^2 k_BT\mu d^2}{\cancel{h^2}}}{\frac{[2\pi m_A k_BT]^{3/2}}{\cancel{h^3}}\frac{[2\pi m_B k_BT]^{3/2}}{\cancel{h^3}}} e^{-E_A/k_BT}$$

$$= \cancel{k_BT}\left(\frac{m_A+m_B}{m_A m_B}\right)^{3/2}\frac{1}{\cancel{2\pi k_BT}}\frac{1}{\sqrt{2\pi k_BT}} \overset{4}{\cancel{8}}\pi k_BT\mu d^2 e^{-E_A/k_BT}$$

$$\frac{1}{\cancel{\mu}\sqrt{\mu}\,2\pi k_B} \cdot 4\pi\, k_BT\cancel{\mu}d^2 e^{-E_A/k_BT}$$

$$\sqrt{\frac{8 k_BT}{\pi\mu}} \cdot (\pi d^2) \cdot e^{-E_A/k_BT}$$

$$\mu = \frac{m_A m_B}{m_A+m_B}$$

$$q^0_A = \frac{1}{h^3}(2\pi m_A k_BT)^{\frac{3}{2}}$$

$$q^0_B = \frac{1}{h^3}(2\pi m_B k_BT)^{\frac{3}{2}}$$

$$q^{\dagger}_{T.S.} = \frac{(2\pi(m_A+m_B)k_BT)^{\frac{3}{2}}}{h^3}\frac{8\pi^2 k_BT\mu d^2}{h^2}$$

So, we have got all the components that I wanted, I have got the transitional, reactants partition functions and the transitional state function. So, let us plug it all in here and see what happens. The transition state is 2 pi, I have to be very very careful because I am, might make mistakes.

So, you also look very carefully and see if I am making a mistake to the power of 3 half divided by h cube into 8 pi square kBT mu d square divided by h square, whole thing divided by qA naught which is 2 pi mA kBT divided by h cube, 2 pi mB kBT divided by h cube 3 half e to the power of minus EA over kBT.

You will see that some terms will cancel for us. First thing I have written something wrong, so let me correct it, the h is simply cube, the bracket should be only here that you can quickly verify that what I have written was wrong. So, h cube cancels with this h cube, this h into h square is h cube, so this also cancels with this h cube.

One of the 2 pi kBT cancels, they all have, both have power of 3 half. So, let me write what I am left with very very carefully. I am left with kBT, I am left with mA plus mB divided by mA mB to the power of 3 half. So, I have a mA and mB here that I have taken out, what I will do is I will write this as 1 over 2 pi kBT into 1 over square root of 2 pi kBT, (())(13:46) soon see why it will just help me in I will delete that arrow it is going to come in between, 8 pi square kBT mu d square into the exponential.

I think I have all the terms, I have kT here, I have mA plus mB divided by mA into mB, I have 2 pi kBT to the power of 3 half here, I have 8 pi square kT mu d square, everything here. So, let us cancel more terms. kT cancels with this kT, one of the pis cancel, 2 cancels with 8 to give you 4. Excellent.

Now I note this term is nothing but 1 over mu, this is 1 over mu into root mu. mA mB over mA plus mB is mu, so this is 1 over mu to the power of 3 half. So, I write that as mu into root mu. Let me just extent it, 2 pi kBT into 4 pi kBT mu d square, one of the mus will also cancel. I will just take this term and I will reorganize in a particular fashion, I will note that I have a kT in the numerator and a root kT in the denominator. So, I will write that as root kT in the numerator.

I will take 4 and write that as square root of 16 and 16 by 2 is 8, so I will write that as 8 over and I will take the pi as well in the numerator. So, I have 8 pi kT divided by mu into, actually let me not take the pi out, I will leave the pi in there and I will write this as pi d square, you will see why. If you were, you do not already see it. If you have been following the modules, you will see, you will recognize this form very carefully.

So, you can verify that this form in this bracket here is exactly the same, just rearranged. Do you recall this expression from some time before, some memory stirs?

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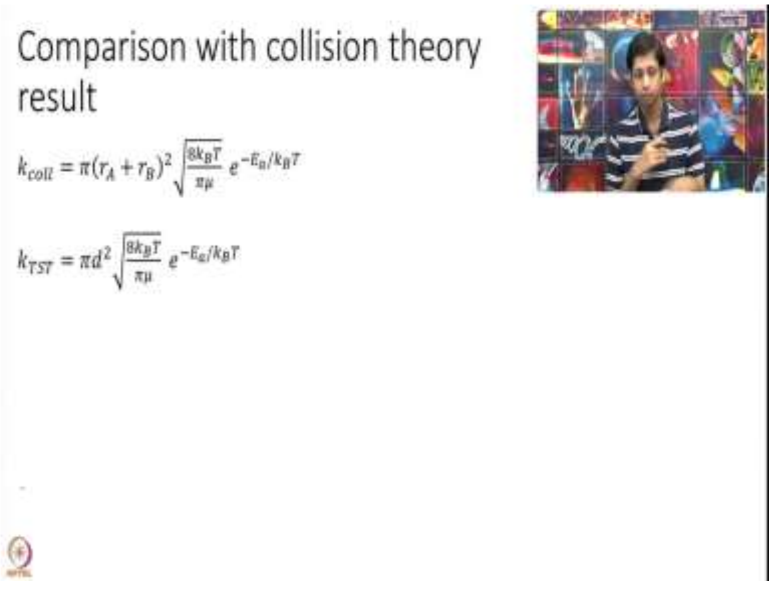

Comparison with collision theory result

$$k_{coll} = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}}\, e^{-E_a/k_BT}$$

$$k_{TST} = \pi d^2 \sqrt{\frac{8k_BT}{\pi\mu}}\, e^{-E_a/k_BT}$$

So, this expression is exactly the same as we derived for collision theory. It was equal to pi, this d was replaced by ra plus rb, but otherwise this was exactly the same. So, what we have got is we have derived collision theory result from transition state theory, so transition state theory is a more general theory than collision theory. So, transition state theory is basically always going to get you better results than collision theory because it is more general, transition, collision theory is a special case of transition state theory.

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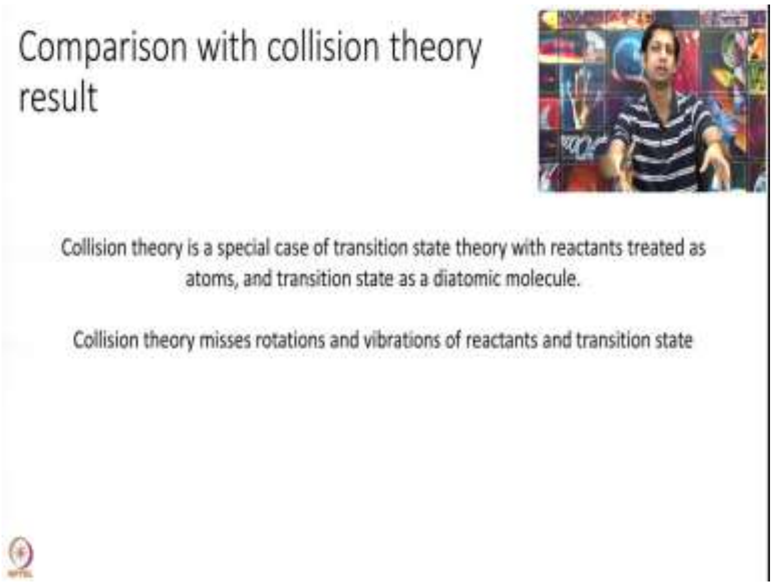

Comparison with collision theory result

Collision theory is a special case of transition state theory with reactants treated as atoms, and transition state as a diatomic molecule.

Collision theory misses rotations and vibrations of reactants and transition state

So, essentially collision theory is a special case for transition state theory applied to two atoms reacting together with a linear transition state that is really what collision theory is and we can derive this collision theory from the way how we derived from the actual mechanics of two (())(17:56) spheres colliding, but you will get the same result out, the fundamentals is the same, so you can think in the language of partition functions and get the same answer out.

So, in effect, collision theory is really missing all rotations and vibrations of my transition state, of my reactants and transition state. And that is what transition state theory is doing, it is looking deeper into the structure of my reactants and transition state and adding appropriate amount of vibrations and rotations as should be added to get you a better rate.

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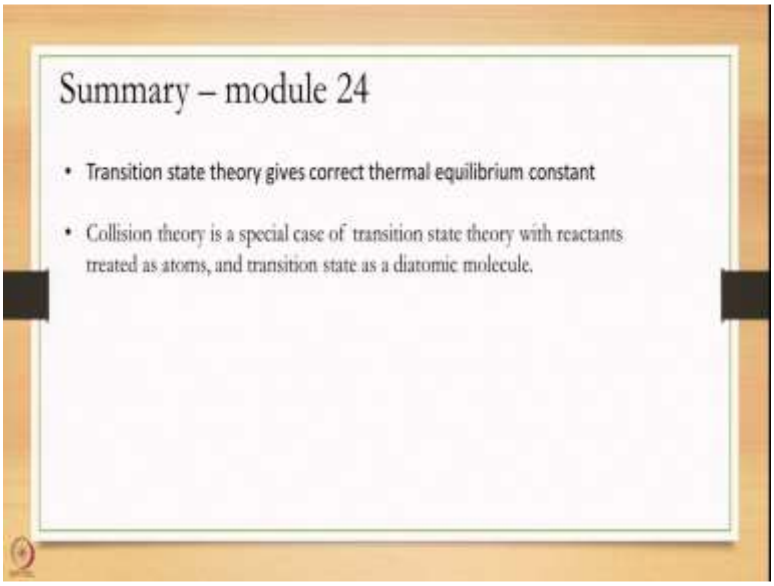

Summary – module 24

- Transition state theory gives correct thermal equilibrium constant
- Collision theory is a special case of transition state theory with reactants treated as atoms, and transition state as a diatomic molecule.

So, in summary, today we have discussed two points, we very briefly looked at the equilibrium constant derived from transition state theory and shown that it is consistent with what you expect from thermodynamics and secondly, we have looked at the relation between transition state theory and collision theory. Collision theory is a special case of transition state theory applied to two atoms colliding together to give a linear transition state. Thank you very much.