Chemical kinetics and transition state theory
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Lecture – 22
Practical Calculation of TST rate

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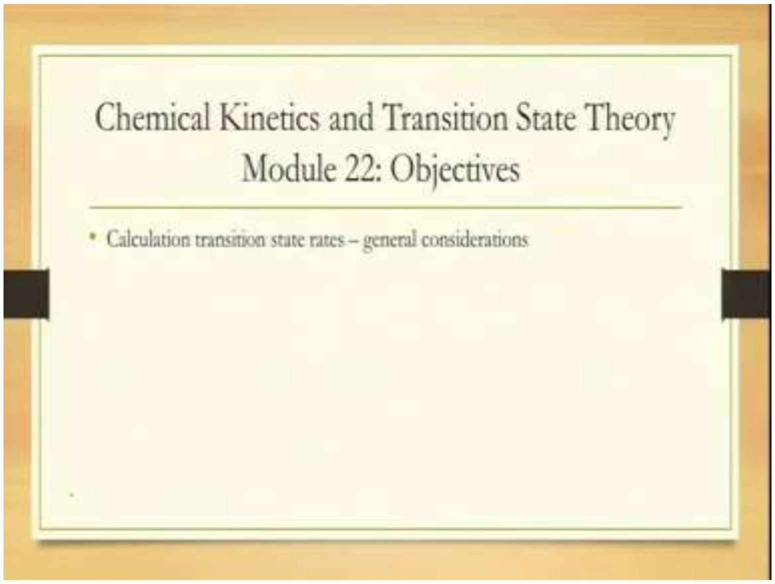

Chemical Kinetics and Transition State Theory
Module 22: Objectives

- Calculation transition state rates – general considerations

Hello and welcome to module 22 of Chemical Kinetics and Transitions State Theory. In the last module we have derived one of the fundamental relations we wanted to derive, which is the calculation of rate constant via transition state theory. So we will spend this module and the next one just looking at some of its numerical, numerical implications.

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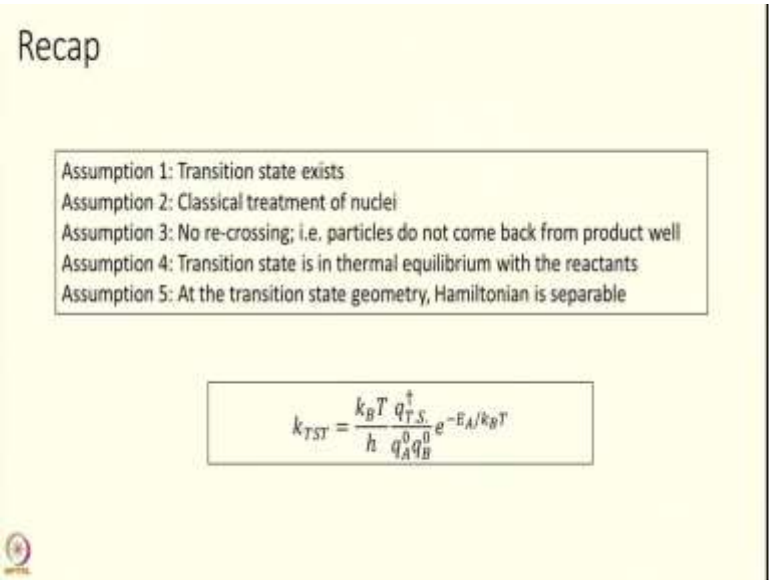

Recap

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

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

So just a quick recap. The transition state rate we derived is given here. So we wrote a formal derivation of this. And this derivation, remember, works under five assumptions. To derive this we have to make five assumptions. One that the transition state exists. Transition state again is the structure which is the maximum energy structure along the reaction path and the minimum energy structure along the coordinate perpendicular to the reaction coordinate.

The second approximation we make is that the, we treat nuclei classically. The third we make that there is no recrossing. That is, we look at the positive flux only. We sit at a transition state and look at all the particles moving forward. We do not see anything coming back. We assume that a transition state is in equilibrium with the reactants.

And finally we assume that, at transition state we have a separability of Hamiltonian, particularly along the reaction coordinate and everything, all other coordinates. Under these five assumptions this relation can be derived, and we did it last module.

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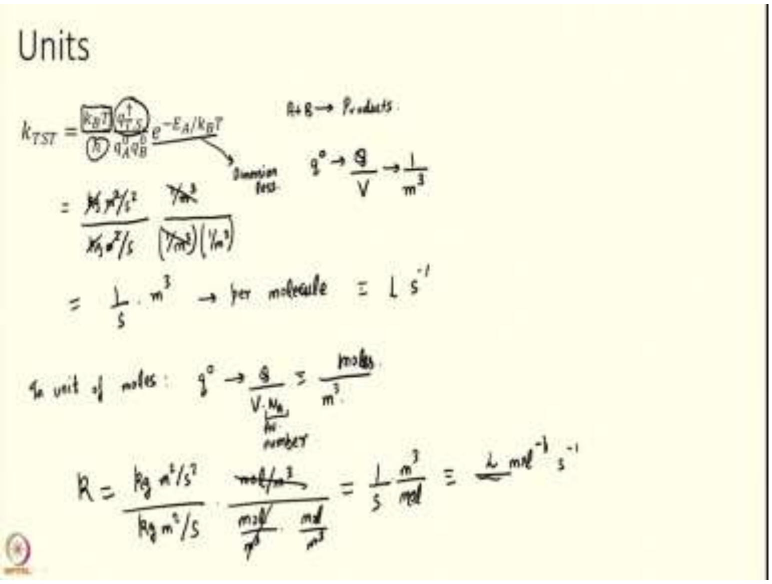


Units

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

A+B → Products

Dimension less

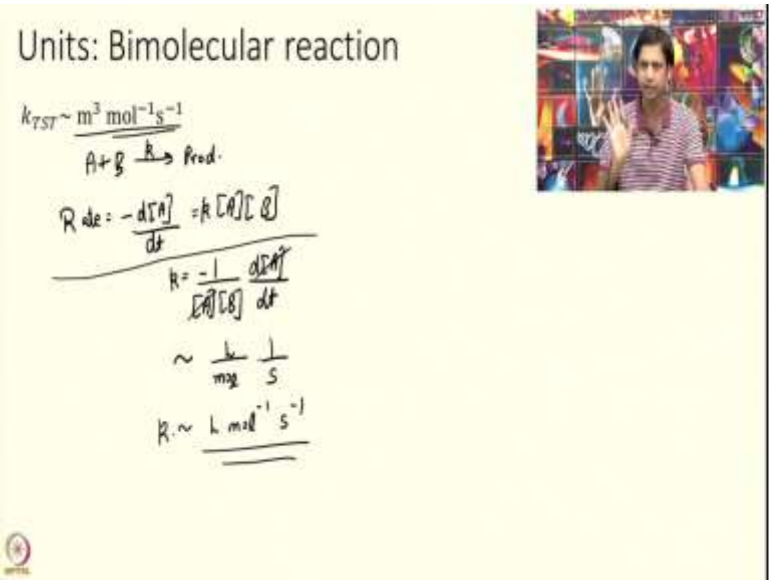
$$q^0 \to \frac{q}{V} \to \frac{1}{m^3}$$

$$= \frac{\cancel{kg}\, \cancel{m^2}/s^2}{\cancel{kg}\, \cancel{m^2}/s} \frac{\cancel{1/m^3}}{(\cancel{1/m^3})(1/m^3)}$$

$$= \frac{1}{s} \cdot m^3 \to \text{per molecule} \equiv L\, s^{-1}$$

In unit of moles: $q^0 \to \frac{q}{V \cdot \underset{\text{Av number}}{N_A}} = \frac{\text{moles}}{m^3}$

$$R = \frac{kg\, m^2/s^2}{kg\, m^2/s} \cdot \frac{\cancel{mol/m^3}}{\frac{mol}{m^3} \cdot \frac{mol}{m^3}} = \frac{1}{s}\frac{m^3}{mol} \equiv L\, mol^{-1}\, s^{-1}$$



Units: Bimolecular reaction

$k_{TST} \sim \underline{m^3\, mol^{-1} s^{-1}}$

$$A + B \xrightarrow{k} \text{Prod.}$$

$$\text{Rate} = -\frac{d[A]}{dt} = k[A][B]$$

$$k = \frac{-1}{[A][B]}\frac{d[A]}{dt}$$

$$\sim \frac{L}{mol}\frac{1}{s}$$

$$k \sim \underline{\underline{L\, mol^{-1}\, s^{-1}}}$$

So let us look at some of its properties of what you we have derived. First, let us try to look at what the unit is. So remember we have made a special case of this relation holds only for a bimolecular reaction. This is not a (())(2:19) requirement. If you have more reactants you just change the denominator. But nonetheless let us stick to bimolecular for a little while. And I want to understand what is the unit of the rate constant I have got. I just want to do sanity check.

So let us look. kB into T is of units of energy. h is units of kilogram meter square per second, basically energy into time. Partition function, what is the unit of this partition function? The partition function, remember, is dimensionless. But this q that is written here is partition function per unit volume.

So remember we had to divide by volume to get to the rate constant and that is how equilibrium constant is also defined. So this has the units of 1 over volume which I will just write as meter cube or liter whichever is your preferred one. So in the numerator I have 1 over meter cube divided by qA naught is 1 over meter cube. qB naught is 1 over meter cube. And this thing is dimensionless.

So this cancels with this and kilogram cancels, meter square cancels. I am left with 1 over second. I take meter cube to the numerator. So I get volume divided by time as my unit. We have to be just a bit careful. This is correct. However this unit is per molecule, per unit molecule of reaction. This is not in the language of moles.

So if I want to think in the language of moles, if I want to think the reaction rate happening per mole then basically you have to rethink of your q naught. That is given by Q over V into NA. We discuss this in a previous module. And so this becomes unit of 1 over meter cube into moles. Remember Avogadro number is 1 over mole. So this is your Avogadro number.

So, now k in this unit of moles will again be kT over h, which is kilogram meter square per second square divided by kilogram meter per second, into now, I have to use the unit of moles here, moles per meter cube; divided by mole per meter cube into mole per meter cube. This cancels with one of them. So I am left with 1 over second into meter cube per mole which is unit wise the same as liter into mole inverse second inverse.

That is the reaction rate constant in the language of moles. Without the language of moles what we had got in was liter second inverse. We do not get the mole inverse. This is atom, per atom. Just make a sanity check whether what we have got is right or not, let us just look at, if I have a reaction like A plus B going to product, rate is given by minus, let us say, d A over dt equal to k A into B. So k is 1 over A, 1 over B minus dA over dt.

So dimension wise this is the same as, you see one concentration will cancel, 1 over concentration; concentration is what? Moles per liter; into dt is 1 over second. So this is the same as liter mole inverse second inverse. So you can see that what we are got from transition state for a bimolecular reaction indeed matches the correct units based on our Rate theory. So we have consistency at least. The formula what we have got is sensible, at least dimension wise.

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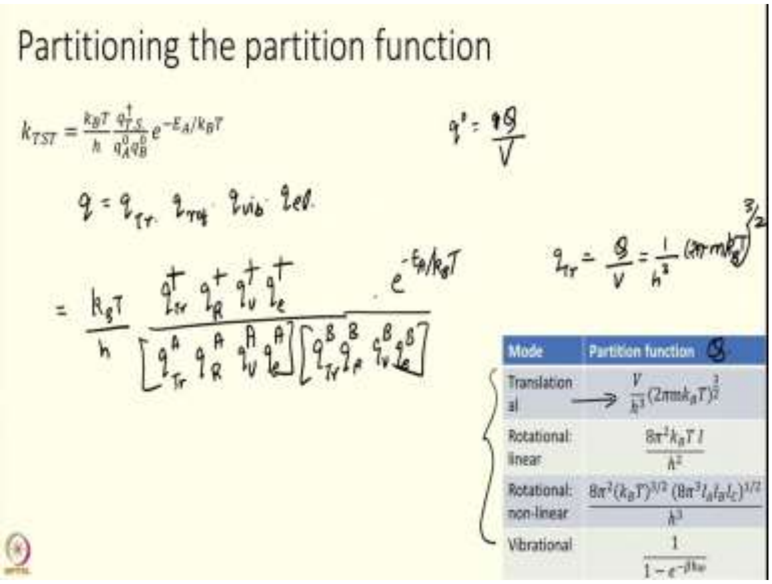


Partitioning the partition function

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

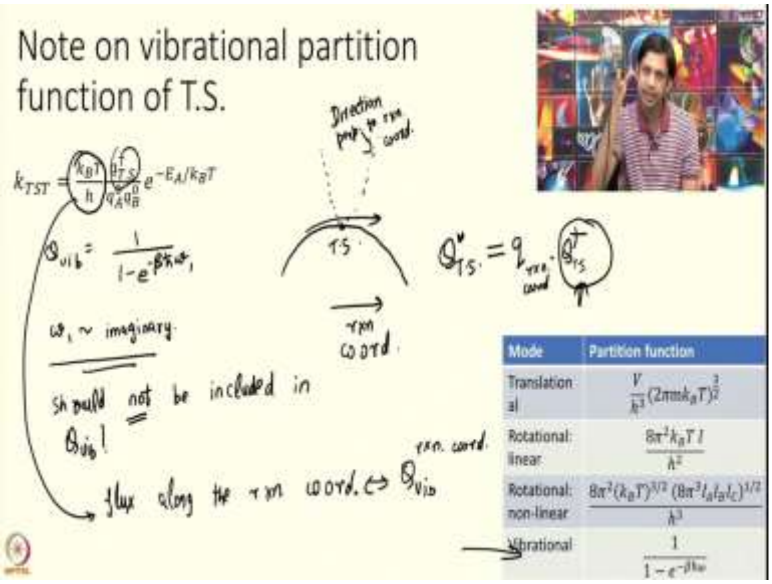
$$q' = \frac{Q}{V}$$

$$q = q_{Tr} \cdot q_{rot} \cdot q_{vib} \cdot q_{el}$$

$$= \frac{k_B T}{h} \frac{q^{\dagger}_{Tr}\, q^{\dagger}_R\, q^{\dagger}_v\, q^{\dagger}_e}{\left[q^A_{Tr}\, q^A_R\, q^A_v\, q^A_e\right]\left[q^B_{Tr}\, q^B_R\, q^B_v\, q^B_e\right]} \cdot e^{-E_A/k_B T}$$

$$q_{Tr} = \frac{Q}{V} = \frac{1}{h^3}(2\pi m k_B T)^{3/2}$$

Mode	Partition function Q
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	$\frac{1}{1-e^{-\beta\hbar\omega}}$



Note on vibrational partition function of T.S.

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

$$Q_{vib} = \frac{1}{1-e^{-\beta\hbar\omega_1}}$$

$$Q^{\dagger}_{T.S.} = q_{rxn\ coord} \cdot \boxed{Q^{\dagger}_{T.S}}$$

$\omega_1 \sim$ imaginary

Should not be included in Q_{vib}!

flux along the rxn coord. $\leftrightarrow Q^{rxn.\ coord.}_{vib}$

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	$\frac{1}{1-e^{-\beta\hbar\omega}}$

Next I just want to discuss how in practice we calculate this answer. What we have discussed already is how we calculate partition functions. And that is basically we divide the partition function into translational, into rotational, into vibrational, into electronic.

We are dealing with the quantum mechanical version now. And we do this division for the transition state for A and for B. And we get our formula as kB T over h q translational, I will use this big cross or dagger for transition state, q rotation dagger, q vibration dagger, q electronic dagger divided by q translation A, q rotation A, q vibration A, q electronic A. And the same will go for B, q rotation B, q vibration B, q electronic B.

So the point is that we calculate each of these quantities one by one. The formula we had looked at before and so again do not go about memorizing these formulas for this course. Wherever the formulas are needed we will give you the formula. So we calculate each component using these formulas and substitute and get the answer. That is the idea. That is how you calculate these kinds of rate constants in Transition State theory.

Just remember to divide by volume. So the volume division we basically take in the translational part. So q translational we take as Q over V which is 1 over h cube into 2 Pi m kB T to the power of 3 half. So the volume is absorbed in the translational part. Remember again, all these qs is the full partition function divided by volume. And what I have listed here is the full partition function.

One important note, about the vibrational partition function of the transition state. So the vibrational component you can see here, at the very bottom here, so q vibrational is given by, what is the problem with transition state? So the transition state, if I zoom in, it looks something like this. So this is my reaction coordinate.

And again transition state is a local maxima there, while this dotted line is a direction perpendicular to; so imagine this coordinate coming out of the screen. So it is perpendicular to the reaction coordinate. So we have a problem actually at the transition state, what looks like a problem at least. One of the frequencies is imaginary. So if you will put, let us say a transition state structure in some electronic structure calculation and ask to do frequency calculations it will give one frequency as imaginary.

So how do I deal with that? Actually it is not a problem at all and we have to actually be careful about it. The point is this mode should not be included in partition, in vibrational partition function. Why is that? So go back to the derivation. The point is, this coordinate, the motion along this coordinate is what we calculated as the flux.

If you look at the derivation once more, what we did was we calculated total number of particles moving per unit time in the forward direction along the reaction coordinate multiplied by the appropriate density, thermal density. That is how we calculated the transition state rate. But, so this direction which has imaginary frequency has been already been included in this factor here.

k T over h is the flux along the reaction coordinate and this is exactly what is incorporated in the q vibration of the reaction coordinate. These are related. So you can go back to the proof very carefully. This partition function along the reaction coordinate, we had intentionally separated. So in the last module we had written q of the transition state is equal to q along the reaction coordinate which we called qr in the last module into q everything else.

So this thing is what enters here in my formula and this does not have the partition function of the reaction coordinate. So the one mode which represents a reaction coordinate, that frequency should not be included when calculating the partition function of the transition state.

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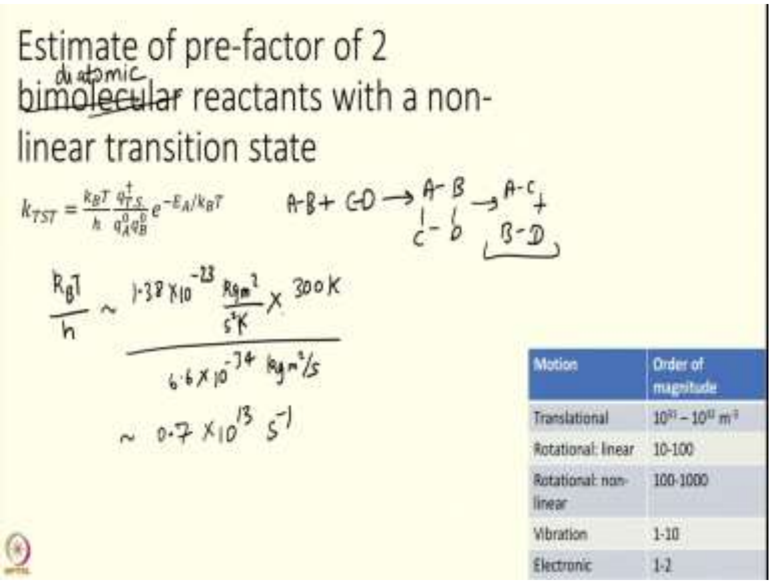


Estimate of pre-factor of 2 ~~bimolecular~~ diatomic reactants with a non-linear transition state

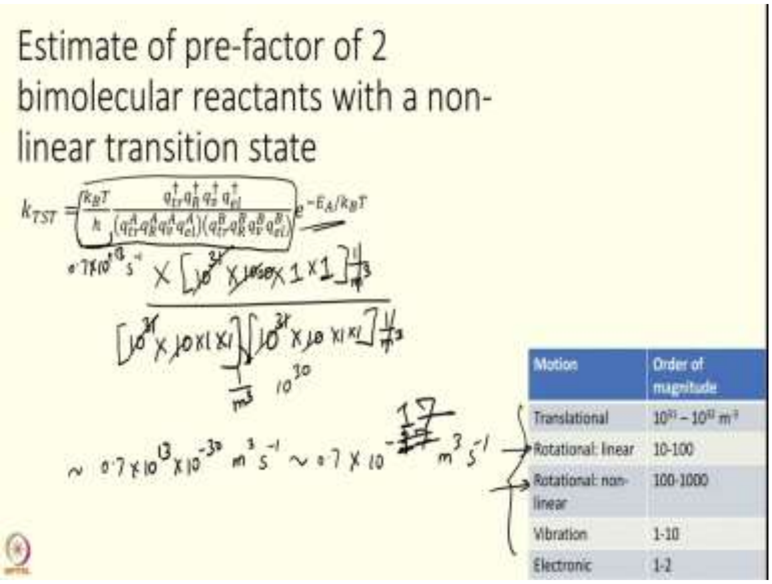
$$k_{TST} = \frac{k_BT}{h}\frac{q^{\ddagger}_{TS}}{q^0_A q^0_B}e^{-E_A/k_BT}$$

$$A\text{-}B + C\text{-}D \rightarrow \begin{matrix} A - B \\ | \quad\ | \\ C - D \end{matrix} \rightarrow \begin{matrix} A\text{-}C \\ + \\ \underbrace{B\text{-}D} \end{matrix}$$

$$\frac{k_BT}{h} \sim \frac{1.38 \times 10^{-23} \frac{kg\,m^2}{s^2K} \times 300K}{6.6 \times 10^{-34}\ kg\,m^2/s}$$

$$\sim 0.7 \times 10^{13}\ s^{-1}$$

Motion	Order of magnitude
Translational	$10^{31} - 10^{32}\ m^{-3}$
Rotational: linear	10-100
Rotational: non-linear	100-1000
Vibration	1-10
Electronic	1-2



Estimate of pre-factor of 2 bimolecular reactants with a non-linear transition state

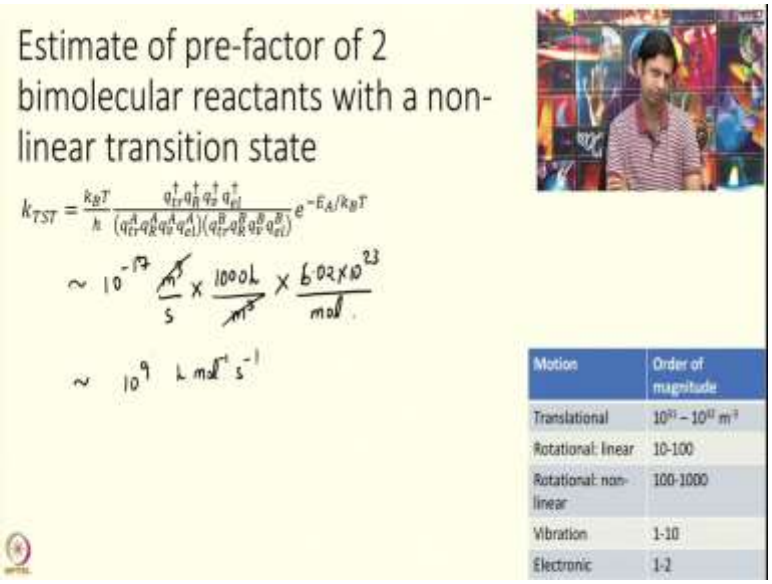
$$k_{TST} = \underbrace{\frac{k_BT}{h}}_{0.7\times10^{13}\,s^{-1}}\frac{q^\dagger_{tr}q^\dagger_R q^\dagger_v q^\dagger_{el}}{(q^A_{tr}q^A_R q^A_v q^A_{el})(q^B_{tr}q^B_R q^B_v q^B_{el})} e^{-E_A/k_BT}$$

$$\times \frac{[10^{31}\times 1000\times1\times1]\frac{1}{m^3}}{[10^{31}\times10\times1\times1][10^{31}\times10\times1\times1]\frac{1}{m^3}}$$

$$\frac{1}{m^3} \quad 10^{30}$$

$$\sim 0.7\times10^{13}\times10^{-30}\ m^3 s^{-1} \sim 0.7\times10^{-17}\ m^3 s^{-1}$$

Motion	Order of magnitude
Translational	$10^{31} - 10^{32}\ m^{-3}$
Rotational: linear	10-100
Rotational: non-linear	100-1000
Vibration	1-10
Electronic	1-2



Estimate of pre-factor of 2 bimolecular reactants with a non-linear transition state

$$k_{TST} = \frac{k_BT}{h}\frac{q^\dagger_{tr}q^\dagger_R q^\dagger_v q^\dagger_{el}}{(q^A_{tr}q^A_R q^A_v q^A_{el})(q^B_{tr}q^B_R q^B_v q^B_{el})} e^{-E_A/k_BT}$$

$$\sim 10^{-17}\frac{\cancel{m^3}}{s}\times\frac{1000L}{\cancel{m^3}}\times\frac{6.02\times10^{23}}{mol}$$

$$\sim 10^{9}\ L\,mol^{-1}s^{-1}$$

Motion	Order of magnitude
Translational	$10^{31} - 10^{32}\ m^{-3}$
Rotational: linear	10-100
Rotational: non-linear	100-1000
Vibration	1-10
Electronic	1-2

So today I will not compute numbers but just make estimates. The next module is dedicated in doing an exact example. We will actually calculate numbers. Today I just want to get a sense of it. So let us just make one quick calculation and make estimates.

So imagine I have two bimolecular reactants, biatomic, diatomic sorry. A-B plus C-D, let us say the transition state looks something like this, going to A-C plus B-D, some reaction like this. I actually do not care what is the product. And I ask you can you give me a ballpark estimate of what the transition state rate is going to come out.

So let us do that. First we calculate what is k T over h. So k T over h is of the order of 1.38 into 10 to the power of minus 23 kilogram meter square per second square Kelvin into let us say, room temperature. That is h. So if I just make a ballpark estimate; you should start doing such kind of calculations on your own. You will get something in the order of roughly maybe half, roughly maybe perhaps 0.7 into 10 to the power of, that is 11, 12, 13 second inverse.

So you can plug it on a calculator, of course and see the answer but it is always more fun to do these kind of ballpark estimates at least just with your head. I just took the powers, 10 to the power of minus 34 goes to the numerator; and I have 34 plus 2 is 36; 36 minus 23 is 13. And roughly this is 0.7 ish.

So that is k T over h. What about the partition functions now? So I have broken the partition functions into translation, rotation, vibration and electronic. And you should actually keep a, once you start doing, practicing these problems on your own, you will anyway get an order; but these are the orders. And we discussed these orders sometimes before as well. Keep like these orders with you. They will help you.

So if I do this ballpark calculation; for the transition state, the translational function is let us say, 10 to the power of roughly 31; rotation it is nonlinear. I do not know what I will use. I will just use 1000 perhaps, 100 to 1000, something in that order. Vibration is roughly going to be around 1. And electronic is usually around 1.

So same thing will happen here. This one is linear A, into 1 into 1, just rough ballpark. I am not being very accurate here, okay, so something in that order. A factor of 10 here and there is fine. So just let me cancel this. This was in the unit of 1 over meter cube, 1 over meter cube. And this is also one over meter cube. 1 over meter cube cancels with this. And I am simply estimating the prefact, pre-exponential which is this.

This thing can change a lot depending upon what your activation energy is, depending on the problem. So again let us try to estimate this. I will take this 10, take this 10, and cancel two zeroes there. I have a 10. So I will take this 10. And get this as 10 to the power of 30. So I have 10 to the power of roughly, 0.7 into 10 to the power of 13 into 10 to the power of minus 30, which is roughly of the order of sorry, 20, 17, okay, so ballpark, let me write this clearly, 17.

Again, so the rate constant is roughly of the order of 10 to the power of minus 17 meter cube second inverse. Let us also convert it into units that are usually reported. So what I have got is 10 to the power of minus 17 meter cube per second inverse. So if I want to convert it into unit of liters and moles. So we just discussed how to go to the units of moles per liter.

So this one will be roughly of the order of; I have 23 plus 3 is 26; 26 minus 17 is 9. So in the units of liter mole inverse second inverse which is much more common unit to be used, we get something in the order of 10 to the power of minus 9, ballpark. You can have a factor of 10 here and there very easily. So this is the kind of numbers you should expect when you are dealing with bimolecular reactions, the pre-exponential factor.

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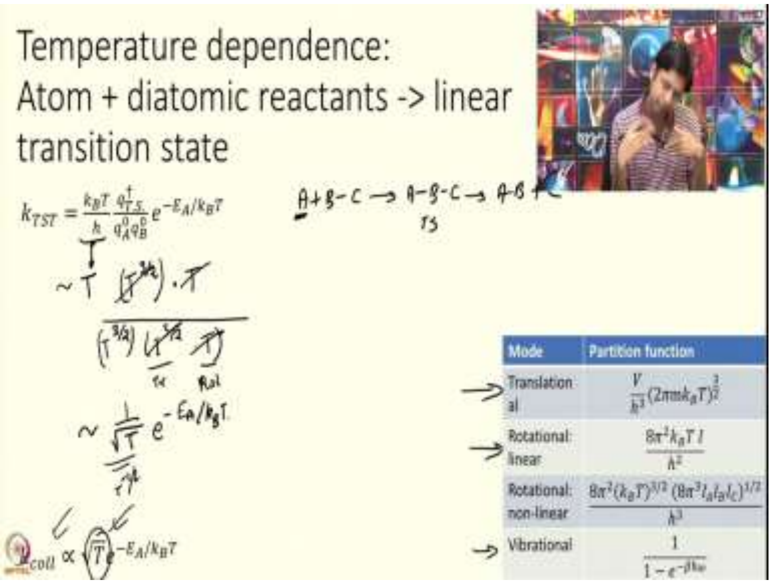

Temperature dependence:
Atom + diatomic reactants -> linear transition state

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

$$\sim \frac{T\,(\cancel{T}^{3/2}) \cdot \cancel{T}}{(T^{3/2})\,\underbrace{(\cancel{T}^{3/2})}_{tr}\,\underbrace{\cancel{T}}_{Rot}}$$

$$\sim \frac{1}{\sqrt{T}} e^{-E_A/k_B T}$$

$$T^{1/2}$$

$A + B\text{-}C \rightarrow \underset{TS}{A\text{-}B\text{-}C} \rightarrow A\text{-}B + C$

$$k_{coll} \propto \sqrt{T}\, e^{-E_A/k_B T}$$

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	$\frac{1}{1-e^{-\beta h\nu}}$

Another thing I just want to quickly point out is the temperature dependence we have got. So imagine, again we can discuss different examples. But imagine if I have some A plus B-C going to A-B C as the transition state, going to let us say, A-B plus C. How will the pre-exponential depend on temperature? Actually, if you go back several modules we have show what is the pre-exponential factor for collision theory.

It looks like root of T into exponential of minus EA over k T. So what will happen for transition state theory is the question? So let us estimate this. I am just looking temperature factors, not constants. So I have a temperature coming from here. Now the transition state for A, for transition state I am assuming to be linear. So for the linear transition state you will have a translational partition function as this, from here. The rotation is linear, so I get multiplied by T.

And basically the vibrational part and the electronic part I will assume to be temperature independent, because usually the frequencies are very high. So to a good approximation I can simply assume that vibrational partition functions are not temperature-dependent, typically. So I do the same thing for A. A is simply one atom. So it has only translation.

Remember that in atom cannot rotate, cannot vibrate, an atom can only translate. I can also have a electronic partition function but that I am assuming has no temperature dependence, approximately. And B-C will have rotation and everything but I will have, this is translation, this is from rotation. So this cancels with this. This cancels with this.

So what I am left with is 1 over root of T into e to the power of minus EA over k T. So you notice that result of transition state estimate in fact does vary from Collision theory, even qualitatively, it is not just getting numerics. You see that the temperature dependence is not exactly the same. Here I got T to the power of minus half compared to the T to the power of plus half. So it is an important thing to note.

And going beyond, actually the transition state estimate will depend on the kind of reaction. So again if I go back to the previous example of A-B plus C-D going to some A B C D, there the dependence will be again different. So the Transition State theory actually looks into molecules more closely. It thinks about vibrations and rotations much more deeply and gets a better estimate actually.

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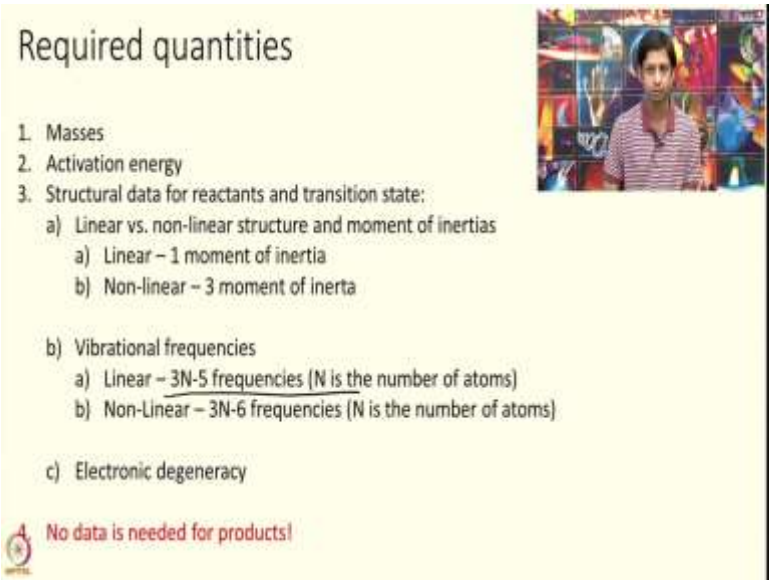

Required quantities

1. Masses
2. Activation energy
3. Structural data for reactants and transition state:
   a) Linear vs. non-linear structure and moment of inertias
      a) Linear – 1 moment of inertia
      b) Non-linear – 3 moment of inerta

   b) Vibrational frequencies
      a) Linear – 3N-5 frequencies (N is the number of atoms)
      b) Non-Linear – 3N-6 frequencies (N is the number of atoms)

   c) Electronic degeneracy

4. No data is needed for products!

So I just want to end today with, if I give you a reaction and I want you to make estimate of the Transition State theory of the rate constant, what are the quantities that you will need to find out for the reaction? So you will need of course the masses of the different atoms involved. You will need the activation energy. Now to calculate partition function, you need the translational partition function which requires a mass. You need the rotation partition function which requires the moment of inertia as well as knowledge whether the molecule is linear or not.

So we have different formula for linear and nonlinear. So you need to determine whether the molecule is linear or nonlinear and then find the corresponding moment of inertias both for reactant and transition state, all reactants that I have and the transition state. And finally you will need to find the vibrational frequencies.

So again we can do the math. The total number of coordinates is 3N plus 6, sorry 3N. For a linear molecule I get 2 rotations. And I always 3 translations. So for a linear molecule I have 3N minus 5 vibrations. So you will need 3N minus 5 frequencies here, for linear. For nonlinear you will need 3N minus 6 because there are 3 rotations and 3 vibrations giving you a total of 6 rotations plus vibrations, sorry, rotations plus translation. So the vibration left is 3N minus 6.

So these frequencies you will have to calculate. They generally come about from either an IR spectra or electronic structure calculation, all these quantities actually. They either come from spectroscopy or from electronic structure. One note again, for transition state you need one frequency less. One frequency will come out imaginary. That frequency is discarded. So for linear we will have 3N minus 6 frequencies. And for nonlinear we will have 3N minus 7 frequencies at the transition state.

Finally we will need the electronic degeneracy of each reactant and the transition state. One important note, no data is required for the products. Whatever is the product forming is independent, it does not determine the rate at all in Transition State theory. That is of course, an approximation. And that approximation has to do with the fact of no recrossing. That we will look at later. So with that I end here.

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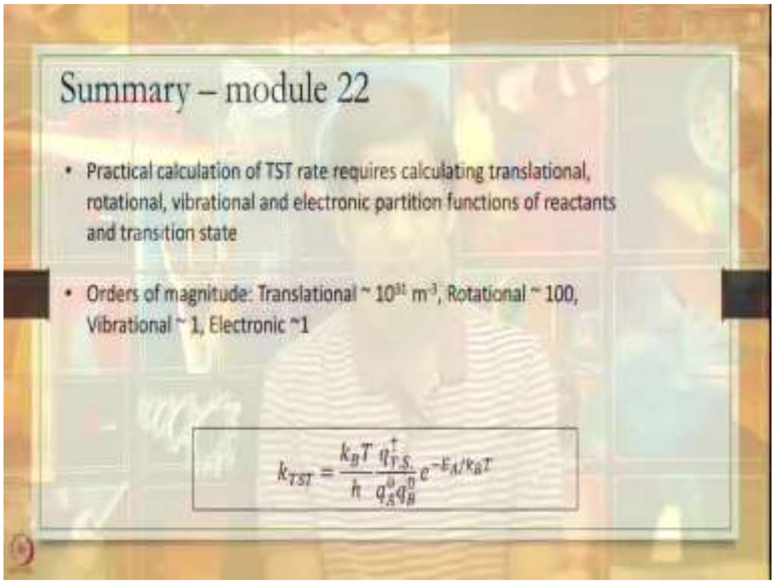

Summary – module 22

- Practical calculation of TST rate requires calculating translational, rotational, vibrational and electronic partition functions of reactants and transition state
- Orders of magnitude: Translational ~ 10^{31} m^{-3}, Rotational ~ 100, Vibrational ~ 1, Electronic ~1

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

Today we have essentially looked at more general discussion of how to calculate this rate constant that comes about from transition state. We have looked at the units carefully. We have looked at orders of magnitude. Something I want you to keep in your head is that translational partition function is in the order of 10 to the power of 31 meter cube inverse, rotational is something in the order of 100; vibrational, electronic are in the order of 1.

Vibrational can be a bit more, can be 10; electronic is usually around 1. And this is the, the formula that is used for calculating rate constants. We will, in the next module, study a concrete example of calculating rate constant. Thank you.