Chemical kinetics and transition state theory
Professor Amber Jain
Department of Chemistry
Indian Institute of Technology, Bombay
Lecture – 23
Calculating of TST rate for the reaction H+HBr

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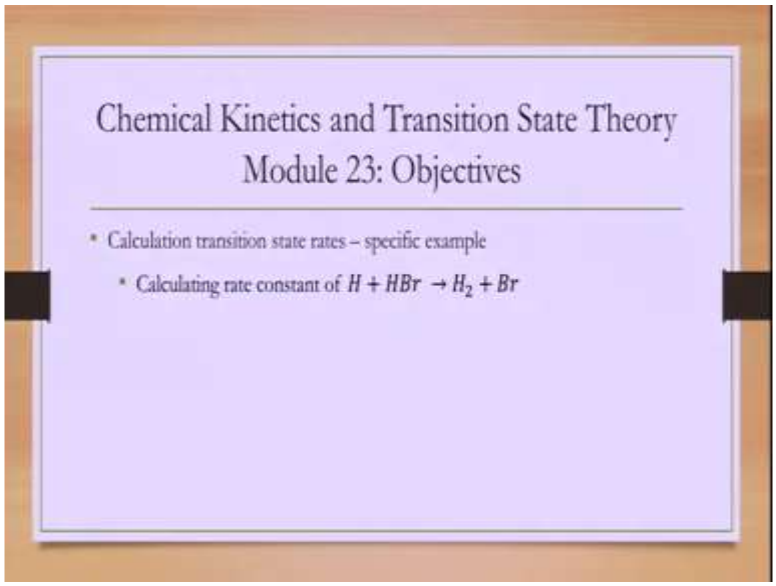

Hello and welcome to module 23 of Chemical Kinetics and Transition State Theory. So now we have a final formula for transition state rate. Today we will look at a specific example on how numbers are exactly evaluated. We will look at the example that we have looked a little bit before anyway, which is H plus HBR going to H2 plus Br. Alright, so let us study this problem. In your assignments you will be solving more such problems for practice.

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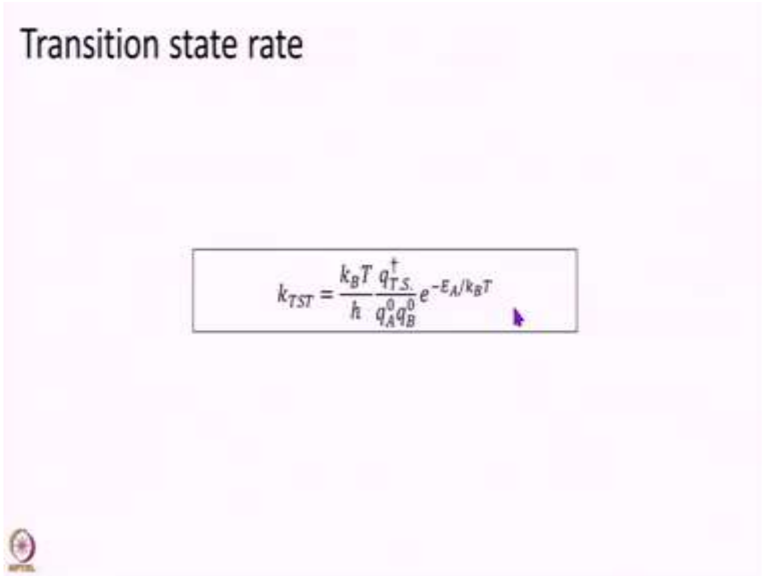

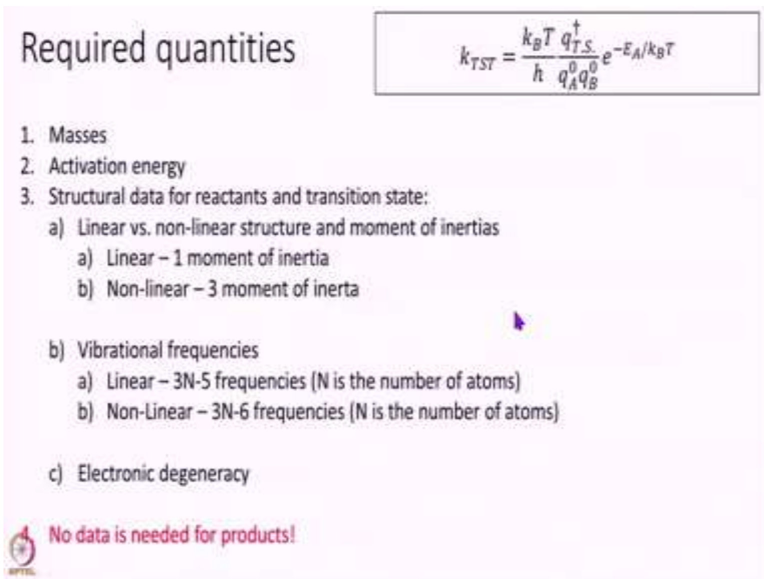

So this is the formula that is what we need to evaluate. So the required quantities that we needed and we discussed this in the last module, so it is a quick recap, is we need all the masses of H and Bagpiper, that is readily available. We will need the activation energy of the reaction. We will need to find whether the reactants and transition state is linear or nonlinear. And what are the corresponding frequencies? We will finally need to look at the electronic degeneracy of the reactants in transition state.

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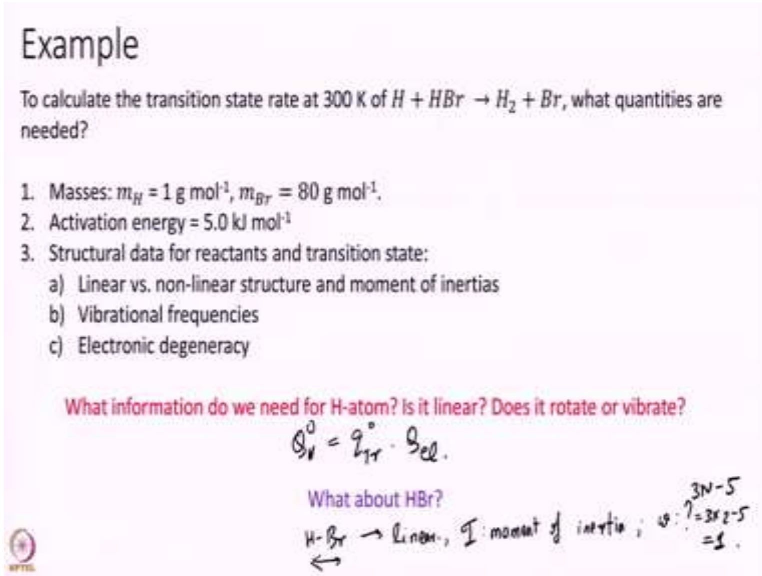

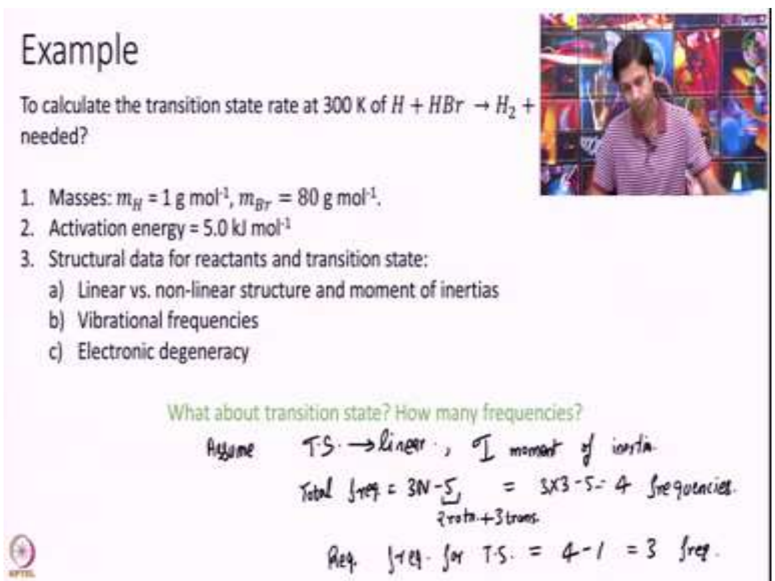

So let us start doing that. The masses we know, 1 gram per mole inverse and 80 gram per mole inverse. That I have just looked up the periodic table. That is all. Activation energy of this problem is known as 5.0 kilo Joules per mole. So we are going to use that. Alright so let us start asking about the structural information. So I have, reactant is H and HBr.

So let us start with H. So the first question I am really trying to ask is, let us say somebody has given you this reaction. Somebody has, experimentalist has done this reaction and you are supposed to find the rate constant. You have to go to your lab and first accumulate all the data. So the question is what all data do you need to find, right? So that is what we are doing.

So far hydrogen atom what all data will you accumulate is the question? Mass we know. Is there any other information you need for hydrogen atom? So take a moment and think about it. Pause the video if you want and think about this question. So hope that you have thought about it. So the question that you have to answer is well for each reactant we have to figure out whether it is linear or nonlinear. We have to find the moment of inertias correspondingly. We have to find the frequencies.

So is H atom linear or nonlinear? Nothing. H atom is a point. So it has no rotational partition function. It has no vibrational partition function. So, so for H atom a simply q translational into q electronic. An atom cannot rotate or vibrate. Get that concept absolutely clear. Atom is simply a point. What about HBr now though? For that we need any more information other than mass? Yes, we do. So, is HBR linear or nonlinear?

Well, of course it is linear. HBr is simply H-Br. Here only two points and two points can only form a line. So this is certainly linear. So we need its moment of inertia. And how many frequencies do I need for HBr? Only one. Why? Well, one can see that I have only one frequency here. It can really just do this kind of a stretch, right. But if you want to be more mathematical you have 3N minus 5 frequencies where N here is 2. So I want one frequency for the HBr molecule.

What about the transition state? What do I need for that? So let us start. We are going to assume, actually to a good approximation that a transition state is linear. So this is the information I am giving you. So then I need one moment of inertia for the transition state. What else do you need? You need frequencies. How many frequencies is the question now.

Do this calculation very carefully. Think. You have a linear transition state of three atoms. How many frequencies should you get? So, pause the video and get this answer right. So let us discuss. It is linear. So total frequency is 3N minus 5. Why 5? 2 rotations for a linear molecule and 3 translations. So linear molecule can rotate in two ways; like this or like this.

And it can translate in all three directions. So I have written 3 and minus 5. N is 3, 3 atoms. So I get 4 frequencies. However one frequency is imaginary at the transition state. That we do not include in our calculation. So, required frequencies is, for transition state, is always one less. So I should get 3 frequencies corresponding to the transition state out of 4.

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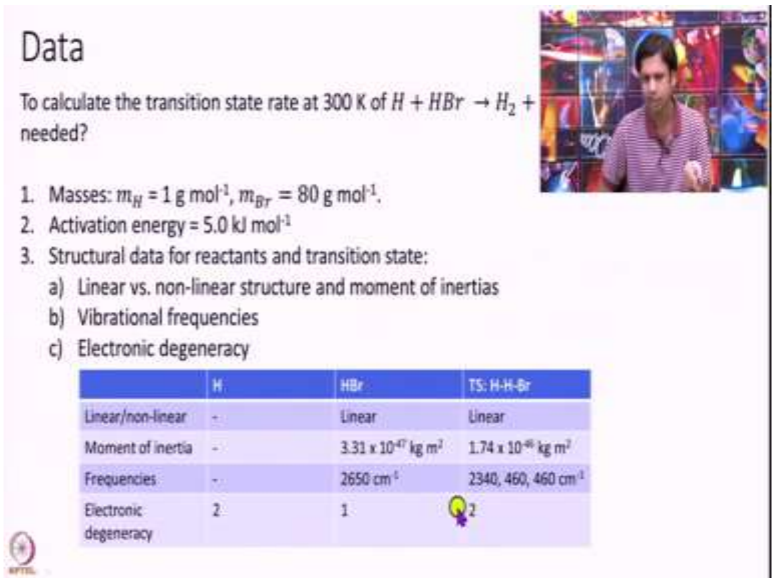

So here is the table where I have provided you all the information. So I did my calculations, I one way or another, by experiment or otherwise, I gathered all the data. In the future module we are going to discuss how this data is exactly tabulated, how by practice do you get it. For the purpose of this course we, whenever data is needed, we will provide you with data. We will not ask you to do the actual experiment.

So we have HBr is, by definition, linear. And we have assumed transition state to be linear. I have provided you the moment of inertia, both of, one moment of inertia because they are both linear. I have provided you one frequency of HBr and three frequencies for HBr, the transition state. H, of course has the degeneracy of 2, electronic degeneracy, because H can be in the positive spin direction or negative spin direction, alpha or beta. HBr has degeneracy of 1.

And transition state I have provided you. It is radical actually. It has a degeneracy of 2, electronic degeneracy of 2.

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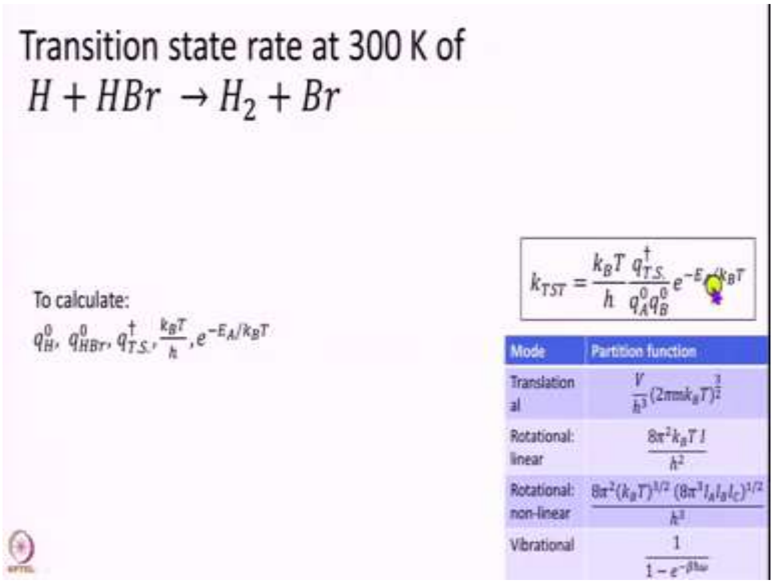

So this is the formula I need. I have all the formulas with me. I will use these formulas. And I may have to calculate basically all the components. I have to calculate kT over h, the three partition functions and this exponential. So that is what we are going to do now.

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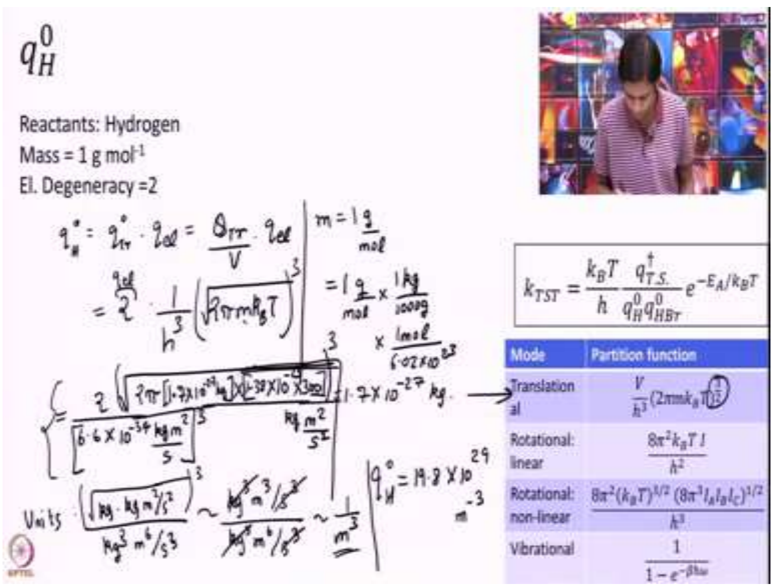

So let us start with qH naught. So the required data I need for qH naught is simply the electronic degeneracy and the mass. qH naught is q translational naught into q electronic which is nothing but q translation divided by volume into q electronic. q electronic is nothing but the degeneracy.

So this is nothing but 2 which is q electronic into q translation over volume. So volume will cancel and I will get 1 over h cube.

I have always to be very, very careful with units. I will be using throughout SI units only. So the mass I need is in kilograms. That is SI unit. What I have is 1 gram per mole. We have done this a few times. 1 gram per mole into 1 kilogram per 1000 gram into 1 mole divided by Avogadro number. So this is equal to 1.7 into 10 to the power of minus 27 kilograms.

So that is the mass I need to put here. So this is then equal to 2 h cube, cube, root 2 Pi, mass is 1.7 into 10 to the power of minus 27 kilograms. kB is 1.38 into 10 to the power of minus 23 into temperature. I am calculating everything at room temperature only. And the unit of k into T will be kilogram meter square per second square.

So let us quickly look at our units. In the numerator I have square root of kilogram into kilogram meter square per second square divided by, in the denominator I have kilogram square, meter six second square, second cube sorry. I have done something wrong. There should be a cube here. My apologies! I am supposed to take the cube of this.

So there is a 3 half. That I had forgotten. That is why my units, you see the importance of looking at units? That is how I figured out I have made a mistake, because I looked at units. So now if I look at it, this becomes kilogram cube meter cube per second cube, divided by, I also had kilogram cube here, meter six by second cube. Kilogram cube cancels. This cancels. So I am left with one over meter cube.

So rest is just plugging in the numbers. I have to just calculate this very carefully on a calculator. And so if I calculate that, I have done that, I get 19.8 into 10 to the power of 29 meter. That is my units, meter minus 3.

So first thing is you get something in the order of 10 to the power of 30. That is what you want. Hydrogen being very light, it usually is a slightly smaller. usually you get 10 to the power of 31. But fine. Hydrogen is light. You get a factor of say little bit lesser. So you get something in the order of 10 to the power of 30. Everything is sensible. My units are correct.

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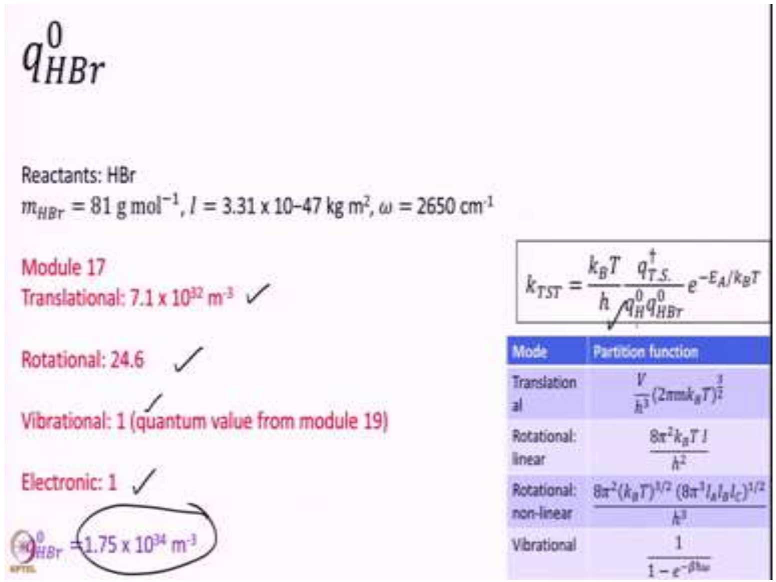

Next, looking at HBr. The data I need will be these following. We need the mass. We will need the moment of inertia and the frequency. And actually for HBr we already have calculated all the components in the previous module. So I am not going to redo it today. You can look back at the previous module.

You can look at module 17 where we actually plugged in the numbers the same way as for hydrogen what we have been doing. And we got for translational 10 to the power 32 roughly. Rotation is roughly of the order of 25. Vibration is very close to 1. Remember we are using the vibrational answer, this answer and not the classical answer.

So that quantum answer we did in module 19. And the electronic is 1 which is the electronic degeneracy of HBr. So if we multiply all these numbers together, I take this into this into this into this. I will get this. So that is the partition function for HBr. So I have done with this. I have done with this.

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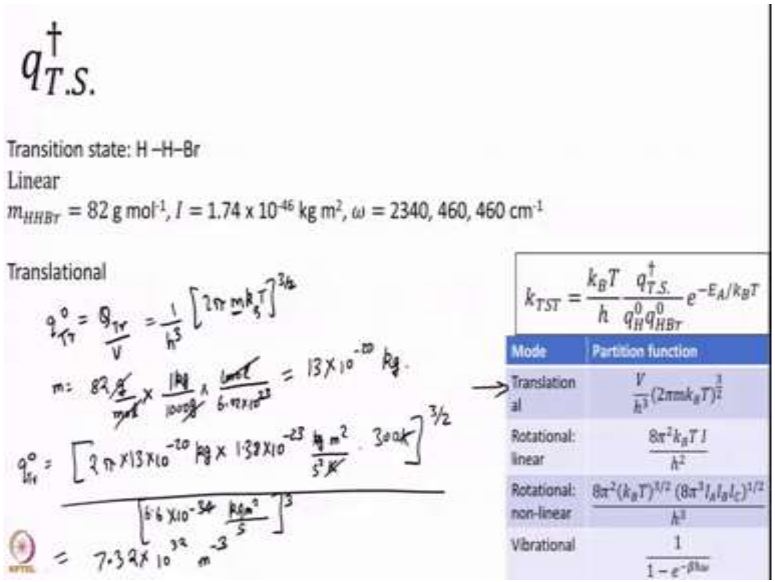

Now moving forward to the transition state we will compute all the three partition functions; translational, rotational and vibrational. So let us start with the translational partition function. So the translational partition function is given here. And so we first of all divide by volume as always. So the translational partition function naught is Q translational by volume. So the volume will cancel. So I will be left with 1 over h cube 2 Pi m k T to the power of 3 half.

So first we need to calculate this m. m is the total mass. So m will be mass of HBr. But what we have to be careful about is units. So this we have to convert in kilograms. And moles is 10 to the power of 23. So mole cancels with mole, gram cancels with gram and I get, I have written the answer here with me. I have calculated this already. So this is simply punching it on a calculator.

So finally I get q Tr naught. Again we have to be just very, very careful with units. 2 Pi, mass is 13 into 10 to the power of minus 20 kilograms into 1.38 into 10 to the power of minus 23, kB is units of kilogram meter square per second square Kelvin, into 300 Kelvin to the power of 3 half divided by h cube. h is 6.6 into 10 to the power of minus 34 kilogram meter square per second cube.

So first thing that I will leave it to you this time is to verify that the units work out correctly. So what is the final unit you should get for qTr? Meter to the power of minus 3. So make sure that is the unit you will actually get here. And all other kilogram, second, Kelvins all everything else is going to cancel. So that I leave it up to you. We have done that a few times now. And the rest, the numbers if I punch in, I get 7.32 into 10 to the power of 32 meter minus 3. So once again in the ballpark of 10 to the power of 31 and 32, so it makes sense.

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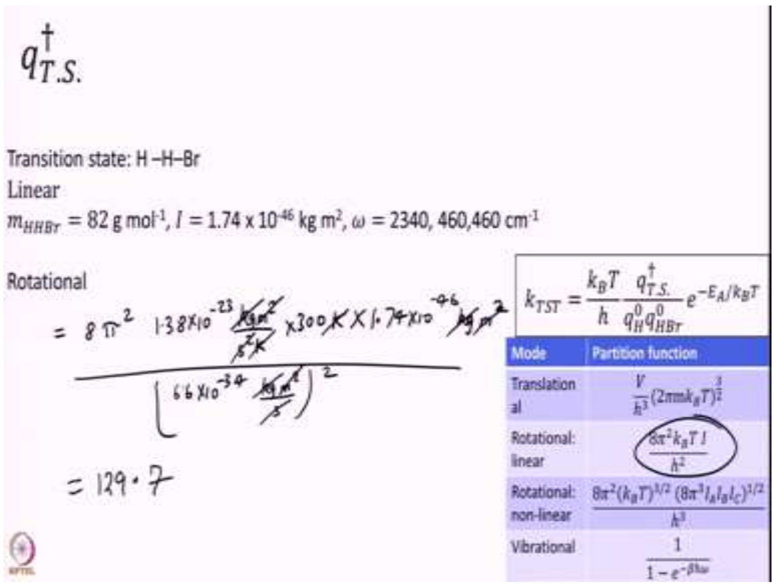

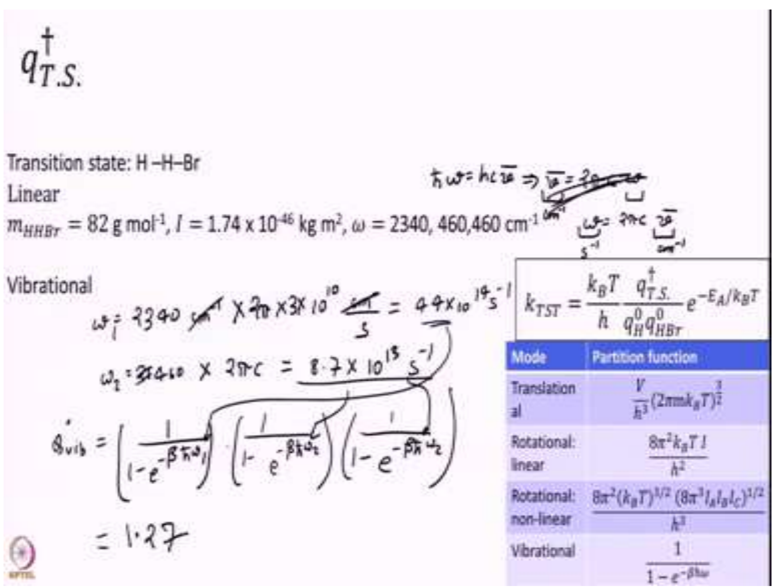

The rotational version, we will use the linear formula. So this is equal to 8 Pi square, kB is 1.38 into 10 to the power of minus 23 kilogram meter square per second square Kelvin, always be careful with units, into moment of inertia is given to be this divided by h square. I have to just write everything very, very carefully and I will be good.

The first thing is all units must cancel; rotation and vibration partition functions are dimensionless. So kilogram into kilogram is kilogram square cancelling the kilogram square in the denominator. Meter to the power of 4 here, meter square, square, 4. Kelvin cancels with Kelvin here. Second square cancels with second square.

Plugging in numbers which comes out to be this. Vibration, I will need the frequencies. So the frequencies note are provided in wave numbers. What we need again are all units in SI units, all quantities in SI units. So I have to go from centimeter inverse to second inverse. Frequency's units are second inverse.

So again the formula I keep in mind is this one. So this is in centimeter inverse, my apologies. Omega equal to 2 Pi c into nu bar. This is in second inverse. This is in centimeter inverse. So I have to multiply by 2 Pi into speed of light. So you know centimeter will cancel. And this comes out to be 4.4. I have written it in my notes here. And 26, my bad, 460. I also multiply with 2 Pi c. And I get, this is simply punching in numbers on a calculator.

So, then what I do is I have to calculate the vibrational partition functions will basically be 1 over 1 minus beta h bar omega 2. And omega 2 actually appears twice. It is degenerate. So that is how you calculate vibrational partition function. You multiply them together. And we are using the quantum version once more. Quantum version is more accurate than the classical version.

So you can plug all these numbers in. You have omega 1 in second inverse. So omega 1 basically will go here. And this will go here. And you know what is your kB, your T, everything. You plug in properly. And you can find this is equal to 1.27, again dimensionless.

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Transition state rate of $H + HBr \rightarrow H_2 + Br$

Transition state: H –H–Br

Translational: $7.32 \times 10^{32}\ m^{-3}$

Rotational: 129.7

Vibrational: 1.27

Electronic: 2

$q^{\dagger}_{T.S.} = 2.42 \times 10^{35}\ m^{-3}$

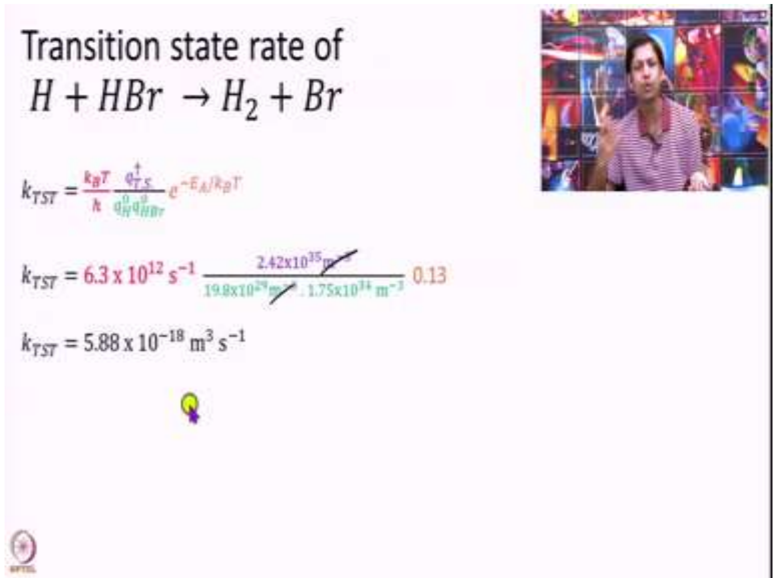
Transition state rate of $H + HBr \rightarrow H_2 + Br$

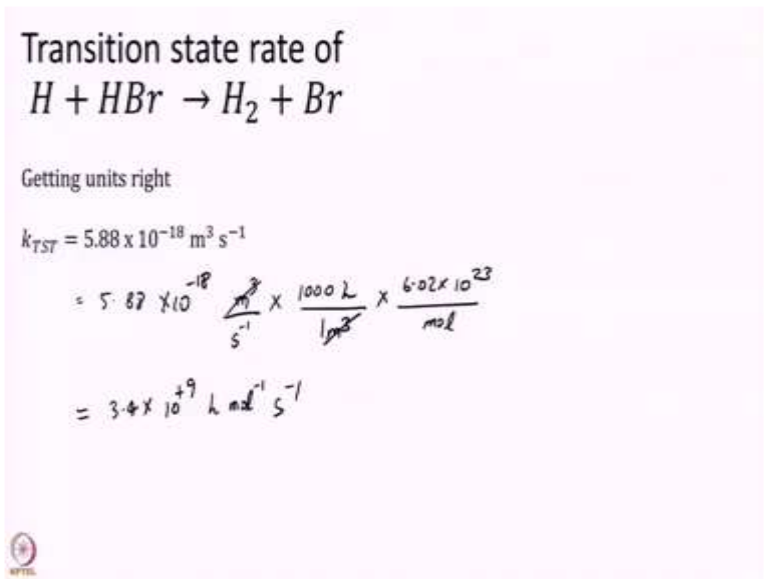
$E_A = 5.0\ kJ\ mol^{-1}$; $R = 8.3\ J\ mol^{-1}\ K^{-1}$

$$e^{-E_A/k_BT} = \exp\left[-\frac{5\ kJ/mol \times 1000\ J/kJ}{8.3\ \frac{J}{mol\,K} \times 300\ K}\right] = 0.13$$

$$\frac{k_BT}{h} = \frac{1.38 \times 10^{-23}\ \frac{kg\,m^2}{s^2 K} \times 300\ K}{6.6 \times 10^{-34}\ \frac{kg\,m^2}{s}} = 6.3 \times 10^{12}\ s^{-1}$$

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





So we have found all the various components now. We have found the translational, rotational, vibrational; and electronic simply the electronic degeneracy which is 2. So I take all of these and multiply them together to get this number here. So I have found the component for translational state as well. Finally we have to calculate the, this exponential factor and k T over h. So k T over h comes here and that is your exponential.

So the exponential is simply minus EA, 5 kilo Joules per mole. I will multiply it by 1000 Joules per kilo Joule because, and kB, instead of using kB I can use R if I want to use per mole unit and temperature I am using this 300 Kelvin. So Kelvin cancels with Kelvin. Kilo Joule cancels with kilo Joule. Joule cancels with Joule. Mole cancels with mole. It is all dimensionless which is what I want. And then you plug it in a calculator and you get, ok finally it is k T over h.

So this is 1.38 kilogram meter square per second square Kelvin. Temperature is 300 Kelvin. Kelvin cancels with Kelvin, kilogram cancels with kilogram, meter square cancels with this and this second cancels with one of the seconds. So I get this is equal to 6.3 into 10 to the power of 12 second inverse.

So finally is the time to plug-in all the numbers together. So I have k T over h which I found to be this. We have found the partition functions. For transition state we found it equal to this. And for h we found this. For HBr we found this. So I have just plugged in the number from the previous slides and exponential I found it to be 0.13.

I multiply them all together. Notice that one of the meter cube cancels. So I am left with meter cube second inverse, and simply punching in into a calculator. So I get rate in the order of roughly 10 to the power of minus 18 meter cube second inverse. Again things you should, like keep sense of. That is how the rates will look like in this unit. So the final thing is let us just calculate in the units of liter mole inverse second inverse. So this will be equal to 5.88 into 1000 liters in 1 meter cube into the Avogadro number per mole.

So you can do this calculation and this comes out to be roughly, oh I have not written this in my note. So I am doing the calculation. You can confirm this, roughly 3.4, 3.4 into 10 to the power of minus 9 liter mole inverse second inverse. I have forgotten to write this actually in my notes, but no issues. This is simply plugging it into a calculator. You can do that and tell me whether I have got it right or not.

So the rates generally are of the order of 10 to the power minus 9 which is what I expect, plus 9 actually, I am sorry, my apologies, this should be plus. But this is simply punching it on a calculator. You can do that better than I can and get that number, alright.

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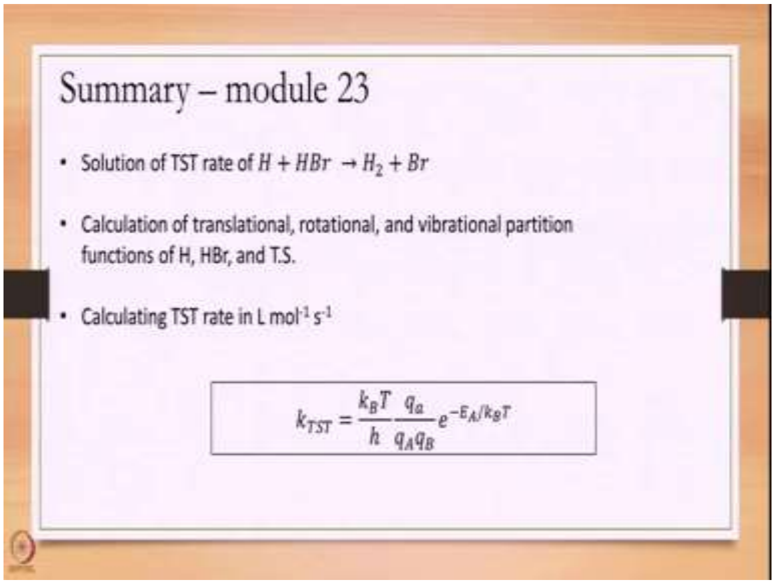

Okay so we end here today. And we have looked at exact calculation of how to calculate it for a specific example which is of H plus HBr with a linear transition state. With, you see, you can use the same procedure to calculate it for any calculation and get the transition state estimate. So the first step is always identifying the parameters you need.

You have to figure out whether the structures are linear or nonlinear, calculate the appropriate amount of moment of inertias, calculate the appropriate frequencies. Always remember that for transition state I require one frequency less. And then plug into the formulas. And after you plug into all the formulas then you have to be just careful with units and get the final answer. Thank you very much.