Chemical Kinetics and Transition State Theory
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Lecture 30
Problem Solving Session 3

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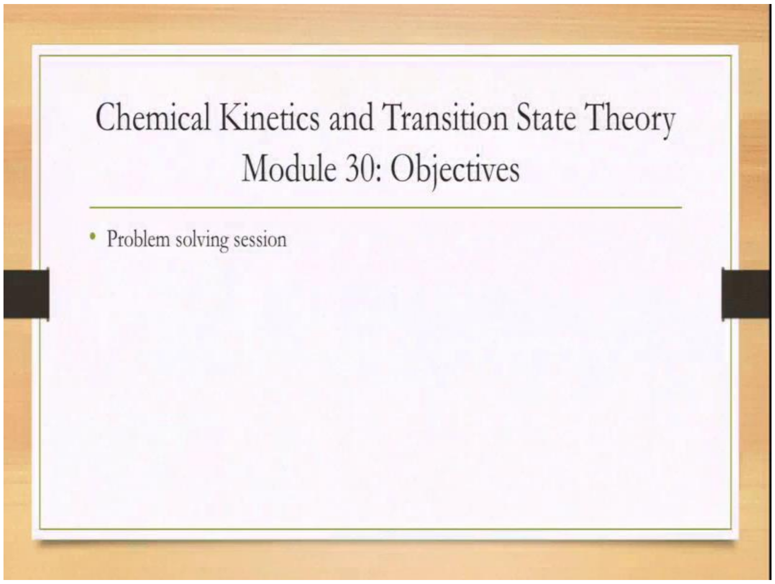

Chemical Kinetics and Transition State Theory

Module 30: Objectives

- Problem solving session

Hello and welcome to module 30 of Chemical Kinetics and Transition State Theory. So, this is going to be kind of the last module directly related to transition state theory. We have covered as much theory as we want to, actually. And today we are just going to solve problems. So, let us start with that. So, let us start with our very first problem.

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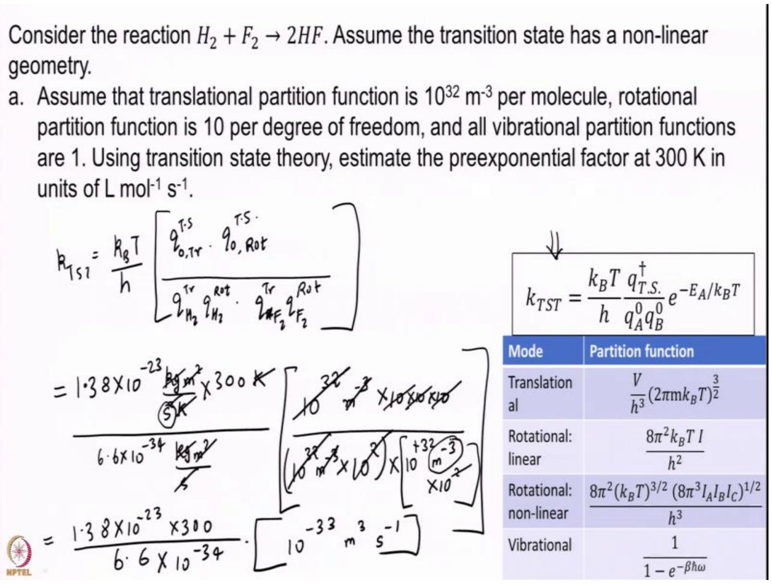

Consider the reaction $H_2 + F_2 \rightarrow 2HF$. Assume the transition state has a non-linear geometry.

a. Assume that translational partition function is 10^{32} m^{-3} per molecule, rotational partition function is 10 per degree of freedom, and all vibrational partition functions are 1. Using transition state theory, estimate the preexponential factor at 300 K in units of L mol^{-1} s^{-1}.

$$k_{TST} = \frac{k_B T}{h}\left[\frac{q^{T.S}_{0,Tr}\cdot q^{T.S.}_{0,Rot}}{q^{Tr}_{H_2}\, q^{Rot}_{H_2}\cdot q^{Tr}_{F_2}\, q^{Rot}_{F_2}}\right]$$

$$= \frac{1.38\times10^{-23}\,\frac{\cancel{kg}\,\cancel{m^2}}{\textcircled{s}\cancel{K}}\times 300\,\cancel{K}}{6.6\times10^{-34}\,\frac{\cancel{kg}\,\cancel{m^2}}{\cancel{s}}}\left[\frac{\cancel{10^{32}}\,\cancel{m^{-3}}\times\cancel{10}\times\cancel{10}\times\cancel{10}}{(\cancel{10^{32}}\,\cancel{m^{-3}}\times\cancel{10^{2}})\times\left[10^{+32}\,\textcircled{m^{-3}}\times10^{\cancel{2}}\right]}\right]$$

$$= \frac{1.38\times10^{-23}\times300}{6.6\times10^{-34}}\cdot\left[10^{-33}\,m^{3}\,s^{-1}\right]$$

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

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, we are going to look at the reaction of H2 plus F2 going to 2HF and let us assume that the transition state is non-linear. So, the first part is that assuming translational partition function is given to be 10 to the power of 32 meter minus 3 per molecule, rotational partition function is 10 per degree of freedom and all other vibrational and electronic partition functions are 1, use TST theory to estimate the pre-exponential factor at 300 kelvin in specific units of liter mole inverse second inverse. So, I really want you to pause this video right now. Solve this problem on your own. This is not a hard problem actually, you should be able to solve this. Pause the video and solve this problem.

Hopefully, you have solved it on your own and you have a number with you. Now we are going to do it together. Pen. Well, as always, whenever formulas are needed, you will be provided formulas. You do not have to memorize formulas, I have provided all the formulas here. It will be up to you generally to figure out which formula will be useful and which formula will not be useful. So, we have to essentially figure out the partition functions.

So, kTST will be equal to kB T over h into the partition functions. So, let us simplify that, partition function of transition state. So that will be Q translational of transition state. I have been using small q, so let me not break my own notation. So, let me use small q only, q naught of transition state, translational into q naught rotational. And since vibrational and electronic are, I am going to assume to be 1 anyway, I will not even bother writing it. This divided by q of H2 translational, q of H2 rotational into q of F2, I am sorry, translational q of F2 rotational. So, this is your pre-exponential. That is what we want to calculate.

So, kB is 1.38 into 10 to the power of minus 23 kilograms meter square per second square kelvin into 300 kelvin, that is the temperature that is given to us divided by 6.6 into 10 to the power of minus 34 kilograms meter square per second, that is h. Q translational per molecule is given to be 10 to the power of 32.

So, transition state is one molecule. So, its partition function is 10 to the power of 32 rotational, so the transitional state is non-linear. How many rotational degrees of freedom are there for a non-linear molecule? Three. So, the rotational will be 10 into 10 into 10. Remember, it is 10 per degree of freedom and I have three rotational degrees of freedom, so I get 10 cube.

H2 translational will be 10 to the power of 32. Now, how many rotations will H2 have? H2 is definitely linear and linear molecule has two rotational degrees of freedom, so I get 10 square. F2 will be exactly the same, 32 meter minus 3 into 10 square. So, let me just pull out my notes. First, we have to make sure that our units are alright. So, kilogram meter square per kelvin, kelvin second, kilogram meter square second.

So, I will be left here with meter cube per second. So, let me just write this thing. 1.38, I have plugged it on a calculator, divided by 6.6 into 10 to the power of minus 34 into 10 to the power of 32 cancels with 10 to the power of 32, I have 10 cube in the numerator, 10 to the power of 4 in the denominator, three of them I can cancel, easy math, minus 33 meter cube second inverse. Second inverse because of this, meter cube because of this.

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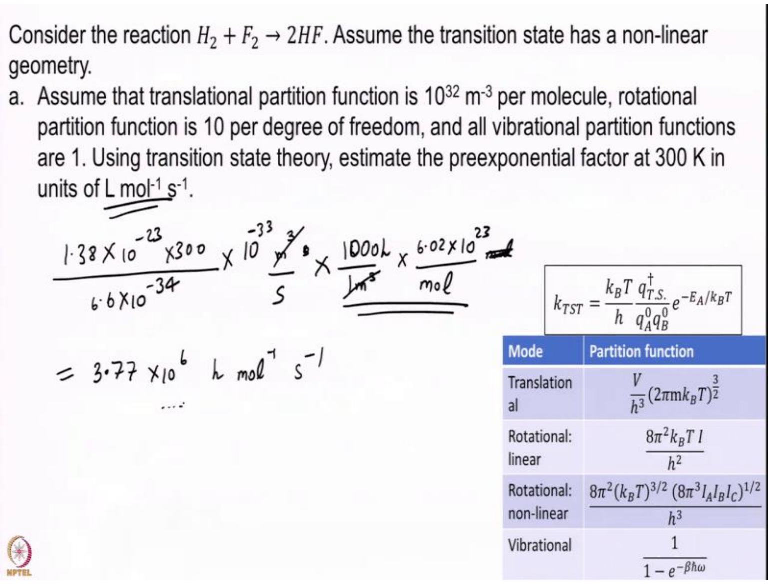

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$$\frac{1.38\times10^{-23}\times300}{6.6\times10^{-34}}\times\frac{10^{-33}\,\cancel{m^3}}{s}\times\underline{\underline{\frac{1000L}{\cancel{1m^3}}\times\frac{6.02\times10^{23}}{mol}}}$$

$$=3.77\times10^{6}\ L\ mol^{-1}\ s^{-1}$$

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

Mode	Partition function
Translational	$\frac{V}{h^3}(2\pi mk_BT)^{\frac{3}{2}}$
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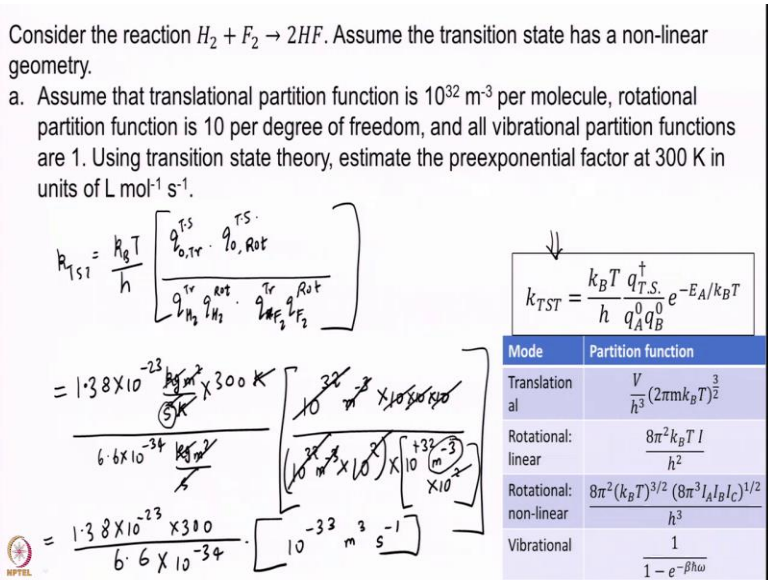

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$$=\frac{1.38\times10^{-23}\times300}{6.6\times10^{-34}}\cdot\left[10^{-33}\,m^{3}\,s^{-1}\right]$$

$$\Downarrow$$

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

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

So, let us write this once more. I have 1.38 into 10 to the power of minus 23, I have forgotten, into 300, sorry, into 300 divided by 6.6, I am sorry, 6.6 into 10 to the power of minus 34 into 10 to the power of 33, minus 33, my bad, sorry for the interruptions, meter cube second inverse. Let me write second like this.

But remember that the unit I want is this, liter mole inverse second inverse. So, we have done this a few times. I am sorry, 1000 liters in 1 meter cube, my pen, in 1 meter cube into 6.02 into

10 to the power of 23 moles, divided by mole. So that is our conversion from per molecule to per mole.

We multiply by the Avogadro number. So, meter cube cancels and I get units of liter mole inverse second inverse. So now it is easy. We just plug it, all of it in a calculator and what I get is, what I have written here, 3.77 into 10 to the power of 6 liter mole inverse second inverse. So this is easy. You have to be just careful of units. You have to remember to multiply by this. If the units asked is liter mole inverse second inverse that is the unit you have to provide the answer in. And look the answer is also somewhat in what we expect. It is a bit lesser. Typically, you get 10 to the power of 8 or 9, but not too far off. So, we have little bit of confidence that we are not completely off the charts.

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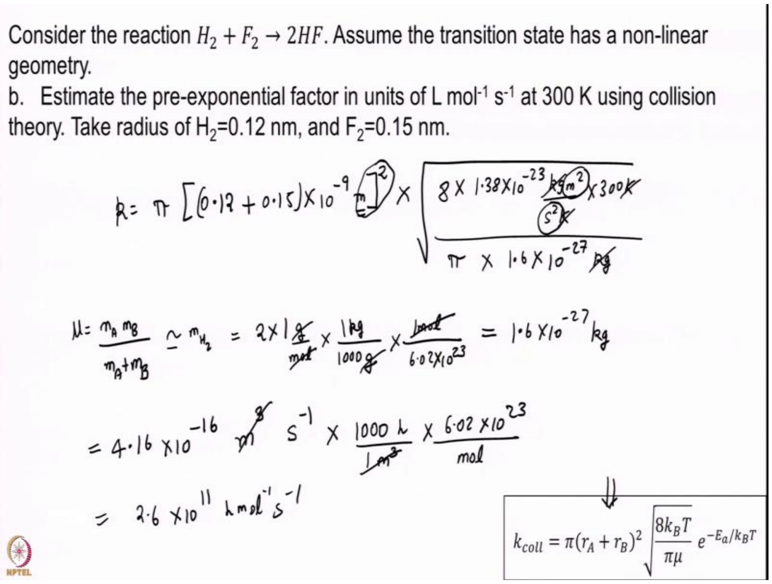

Consider the reaction $H_2 + F_2 \rightarrow 2HF$. Assume the transition state has a non-linear geometry.

b. Estimate the pre-exponential factor in units of L mol^{-1} s^{-1} at 300 K using collision theory. Take radius of H$_2$=0.12 nm, and F$_2$=0.15 nm.

$$k = \pi \left[(0.12 + 0.15) \times 10^{-9}\, m\right]^2 \times \sqrt{\frac{8 \times 1.38 \times 10^{-23}\, \frac{\cancel{kg}\, m^2}{s^2\, \cancel{K}} \times 300\, \cancel{K}}{\pi \times 1.6 \times 10^{-27}\, \cancel{kg}}}$$

$$\mu = \frac{m_A m_B}{m_A + m_B} \simeq m_{H_2} = 2 \times 1\, \frac{\cancel{g}}{\cancel{mol}} \times \frac{1\, kg}{1000\, \cancel{g}} \times \frac{\cancel{1 mol}}{6.02 \times 10^{23}} = 1.6 \times 10^{-27}\, kg$$

$$= 4.16 \times 10^{-16}\, \cancel{m^3}\, s^{-1} \times \frac{1000\, L}{1\, \cancel{m^3}} \times \frac{6.02 \times 10^{23}}{mol}$$

$$= 2.6 \times 10^{11}\, L\, mol^{-1}\, s^{-1}$$

$$\Downarrow$$

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

So now we will look at part b of this problem. Let us recalculate this but from collision theory now. The collision theory if you have forgotten by now, the rate is provided here. So again, take a pause. Solve this problem, get the answer in liter mole inverse second inverse and then come back. So, pause the video now. Hopefully, you are back. Hopefully, have punched the numbers on a calculator and got a number out. Those are very important skills. So, let us calculate it on our own.

So, k will be equal to pi, rA plus rB, rA is 0.12 nanometer plus 0.15 nanometer, but we will write everything in SI units which meter and 1 nanometer is 10 to the power of minus 9 meter into root

8, kB is 1.38 into 10 to the power of minus 23 kilogram meter square second square kelvin into 300 kelvin divided by pi into mu. Mu is the reduced mass, is mA mB over mA plus mB. You can calculate it exactly, but I know that since hydrogen is so much lighter than fluorine, we will just say this is the mass of hydrogen, but you can work it out.

So, the mass of hydrogen will be 2 into 1 gram per mole. But again, we want it in SI units, 1 kilogram per 1000 gram. I am doing all of these problems so explicitly just so that you get used to this notion of units, they are very important. And unless you work them out on your own and keep on listening to me, you will not be able to solve them, you have to practice. So, if plug all of this in, I get 1.6 into 10 to the power of minus 27 kilograms. Moles cancels with mole, gram cancels with gram. So, I will use 1.6 into 10 to the power of minus 27 kilograms here.

If you want to improve, you can use the mass of fluorine as well and calculate what you get exactly, but it would not be very different. So, kilogram cancels with kilogram, kelvin cancels with kelvin. So, if I plug all of this in, I got 4.16 into 10 to the power minus 16 units. Units are, I have meter square here and I get another meter here. So, meter square into this, meter I take the square root, I get meter, so this becomes meter cube second inverse, because I have a second square here. So, if I take the square root of that, I get 1 over second.

But we have to do the same thing as, for transition state. We multiply it by 1000 liters over 1 meter cube into 6.02 into 10 to the power of 23 over moles. So, meter cube cancels her, I get liter mole inverse second inverse. I multiply all of this and I get 2.6 into 10 to the power of 11 liter mole inverse second inverse. So, these are numerics. But one point I want you to now notice.

Notice what we got out of transition state theory. Roughly 4 into 10 to the power of 6. Now notice what I have got out of collision theory, 10 to the power of 11, 5 orders of magnitude more. So, does that make sense? This is not really written as a problem, but now you know transition state theory, you now know collision theory, can you explain this? So, the explanation really is the collision factor in collision theory. In collision theory we have assumed all collisions are equally reactive.

So, when I write this formula here, what I am assuming is that H2 and F2 can come in any orientation and they hit each other and a reaction is going to happen. But you of course know that is wrong. H2 and F2 have to approach in a very special way for the reaction to happen. So

H2 looks like this, F2 looks like this and they have to come like this. If it comes like this, the reaction would not happen. There are only a few orientations where the reaction will be happening. And so as is usual, collision theory will grossly overestimate the rate constant, that is the usual case with collision theory. And now transition state theory has actually corrected for that. You see the transition state theory naturally gave you a much lower rate constant.

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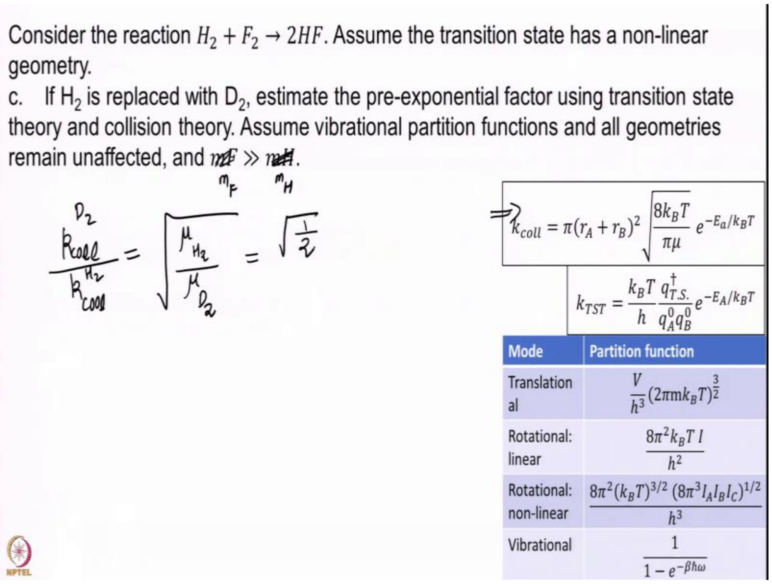

Consider the reaction $H_2 + F_2 \rightarrow 2HF$. Assume the transition state has a non-linear geometry.

c. If H_2 is replaced with D_2, estimate the pre-exponential factor using transition state theory and collision theory. Assume vibrational partition functions and all geometries remain unaffected, and $\overset{m_F}{\cancel{mF}} \gg \overset{m_H}{\cancel{mH}}$.

$$\frac{k_{coll}^{D_2}}{k_{coll}^{H_2}} = \sqrt{\frac{\mu_{H_2}}{\mu_{D_2}}} = \sqrt{\frac{1}{2}}$$

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

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

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	$\frac{8\pi^2 (k_BT)^{3/2}\,(8\pi^3 I_A I_B I_C)^{1/2}}{h^3}$
Vibrational	$\frac{1}{1 - e^{-\beta h\omega}}$

Final problem and this is a hard problem now, but I still want you to think about it at least. If H2 is replaced with D2, can you estimate the pre-exponential factor using transition state theory and collision theory? You can assume vibrational partition functions are independent of mass and you can assume geometries are independent of mass and you can assume that the mass of fluorine is much greater than mass of H. This is m underscore F, my bad, mH, but hopefully you understand that.

So, this is slightly hard. Here you will have to make certain assumptions. I also emphasize that this is slightly open ended without providing you full information. And such a problem I will never give you in an examination setting. Well, but all teaching is not about examinations anyway. So, this is you think about it and then we can discuss it together and I will provide you my thoughts on it. So again, take a pause and first attempt the problem on your own.

Hopefully, you have taken a pause. And you should think on this problem because this is a slightly deeper problem. We will first start with collision theory, that one is actually easy, that one is not very deep. So, collision theory rate is provided here. So, if I have to work with k collision D2 over k collision H2, well, you noticed that first of all, all geometry factors we have assumed to be same. So, things like rA or rB are same. So, they will cancel out. kT will cancel out, pi will cancel out. The only think I will be left with is mu of H2 divided by mu of D2.

Also please note that it is inversely proportional to mu, the rate constant. So, k of D2 over k of H2 is mu of H2 over mu of D2 square root. So, this is easy. I know that mass of deuterium is double of mass of hydrogen, so the reduced mass will also be double. So, I get this as square root of 1 over 2, plain and simple.

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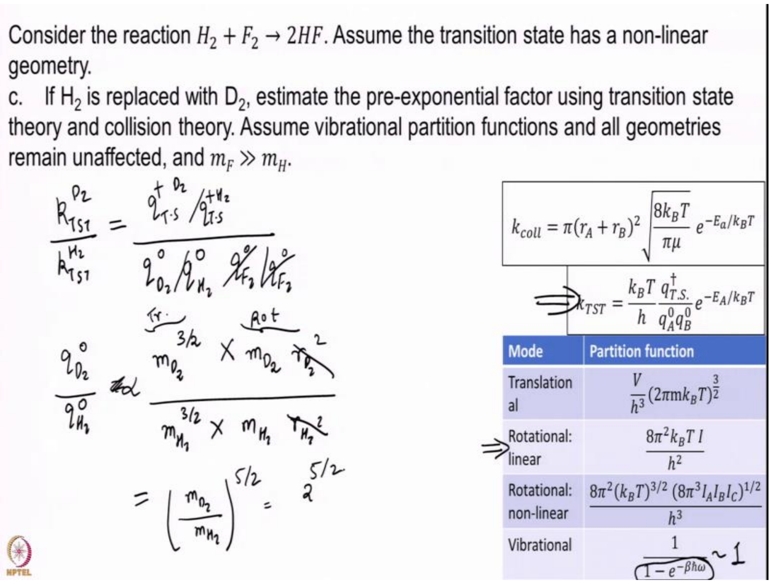

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c. If H_2 is replaced with D_2, estimate the pre-exponential factor using transition state theory and collision theory. Assume vibrational partition functions and all geometries remain unaffected, and $m_F \gg m_H$.

$$\frac{k_{TST}^{D_2}}{k_{TST}^{H_2}} = \frac{q_{T.S}^{\dagger D_2} / q_{T.S}^{\dagger H_2}}{q_{D_2}^0 / q_{H_2}^0 \; \cancel{q_{F_2}^0} / \cancel{q_{F_2}^0}}$$

$$\frac{q_{D_2}^0}{q_{H_2}^0} \propto \frac{\underbrace{m_{D_2}^{3/2}}_{Tr.} \times \underbrace{m_{D_2} \cancel{r_{D_2}^2}}_{Rot}}{m_{H_2}^{3/2} \times m_{H_2} \cancel{r_{H_2}^2}}$$

$$= \left(\frac{m_{D_2}}{m_{H_2}}\right)^{5/2} = 2^{5/2}$$

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

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

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

Now, let us work with transition state theory. That one is slightly more complex, but it is doable. So kTST of D2 divided by kTST of H2. KT over h, now I am looking at this formula. So, kT over h is the same for D2 or H2. The temperature is the same. What I have is q transition state of D2 divided by q transition state of H2 divided by q of D2 divided by q of H2 naught and fluorine is the same. So, this is 1, happily enough and the exponential also cancels. So, we are assuming all energetics remains the same.

So, we have to now find these ratio of partition functions. We will start with qD2 naught over qH2 naught. So, the partition functions will comprise of rotation, vibration, translation and so no and so forth. Vibration we are ignoring and the reason actually why we are ignoring vibration is because frequency is large, so either of D2 or H2 were different, but they are much larger than room temperature none the less and therefore this factor does not matter. This still comes out close to 1. Beta h omega is still much less than 1 and therefore this comes out close to 1 anyway for both D2 and F2, and H2. Therefore, I am ignoring vibrational partition function, but I still have translational and rotational.

So, the translational partition function, I will have m of D2 to the power of 3 half here, all other factors are going to cancel, so I am looking at this 2 pi kT and all that, into the rotational. So, this is translational. Now I have to write the rotational. For the rotational, this is linear. D2 has to be linear, H2 has to be linear. And for linear the moment of inertia will go as mu r square. So, again, this will be proportional to mass, some proportionality constant let us say, m of D2 multiplied by some distance, but distance again we are assuming to be same.

So even if I write D2 square, I do not clear, similarly, I will write this. But we are assuming all distances are equal, so rH2 equal to rD2. So that term cancels. So, I get this as equal to mD2 over mH2 to the power of 5 over 2, which is nothing but 2 to the power of 5 over 2.

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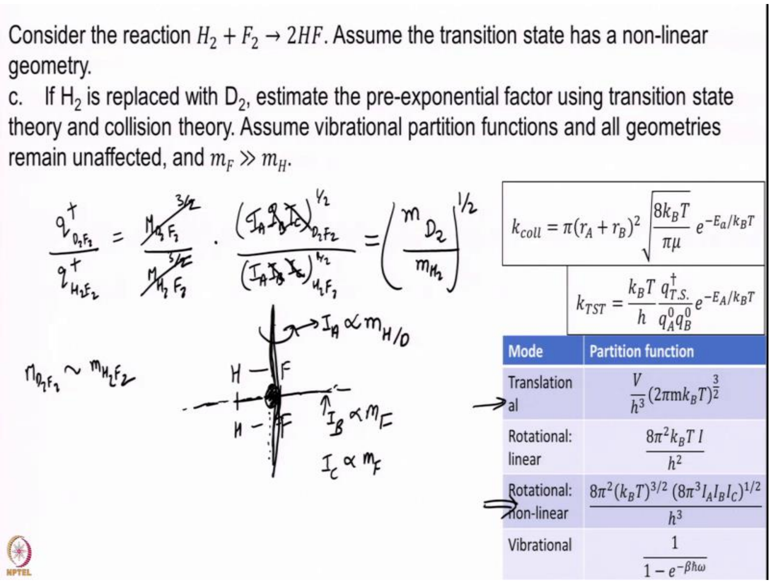

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$$\frac{q^{\dagger}_{D_2F_2}}{q^{\dagger}_{H_2F_2}} = \frac{\cancel{M_{D_2F_2}^{3/2}}}{\cancel{M_{H_2F_2}^{3/2}}} \cdot \frac{(I_A \cancel{I_B} \cancel{I_C})^{1/2}_{D_2F_2}}{(I_A \cancel{I_B} \cancel{I_C})^{1/2}_{H_2F_2}} = \left(\frac{m_{D_2}}{m_{H_2}}\right)^{1/2}$$

$m_{D_2F_2} \sim m_{H_2F_2}$

$I_A \propto m_{H/D}$

$I_B \propto m_F$

$I_C \propto m_F$

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

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

Now, somewhat harder thing to understand is for the transition state, qD2 of the transition state divided by qH2 of the transition state. Again, I will have translation and rotation. Sorry, not D2 and H2, this will be H2F2. Let me clean this up. D2F2 and H2F2. The mass, I have the translational part. Translational part again is here, which is m of D2F2 to the power of 3 half divided by m of H2F2 to the power of 3 half, but note that the mass of fluorine is much more than mass of hydrogen or deuterium. So, to very good approximation I can say that mass of D2F2 is almost the same as mass of H2F2. This is, remember, the total mass. So, I am adding the masses.

So, when I add the mass, if I write H2 which will give you a mass of 2 or if I write D2 which will give you a mass of 4, the difference will be only 2. So, if I take this ratio and I add fluorine as well, remember that and fluorine is very large, so this is almost equal. The hard part is the rotational part. So, this will be IA, IB, IC of D2F2 divided by IA, IB, IC H2F2. Again, we have not discussed much of mechanics in this course, so we have not went into this moment of inertia in a great detail.

But what do these moment of inertia physically represent? They represent three kind of motions. So, let us just think about what this transition state is. You know a little bit of your chemistry. Some structure like this. Now this structure can rotate in three possible ways. So, let us imagine this is my center of mass, I can draw a line like this and rotate the whole thing like this.

I can draw a line like this and rotate about this axis and I have a line going through the plane of my board, through the plane of the screen like this. So those are my three axis and along all three axis I am rotating the molecule. The question is how will moment of inertia change with mass? What is your intuition? So that is slightly open ended. You do not, you can calculate it if you want, but let us try to make educated guesses without doing proper math.

The point is any motion that will involve moving fluorine a lot will require moment of inertia of fluorine atom. But the kind of motion where fluorine is not moving much, assume fluorine is infinitely massive, so in that limit, one axis which is this axis, which is almost passing through the two fluorines, if I rotate around this axis, you see fluorines are not moving, the two hydrogens are moving.

So, the moment of inertia corresponding to this will be proportional to mass of hydrogen or deuterium depending whether the, this is H2 or D2. But if I rotate let us say about this axis, you see this will be dominated by mass of fluorine, because here fluorine is moving. So, this is a slightly more involved concept. But hope it has some sense.

Also, you can think of the third axis which is passing through the screen that also involves rotation of fluorine. So that will also involve rotation of, mass of fluorine. So, I have only one I which will depend on the mass of hydrogen or deuterium. So, this thing will become mD over mH2 to the power of only 1 half. IB will cancel and IC will cancel.

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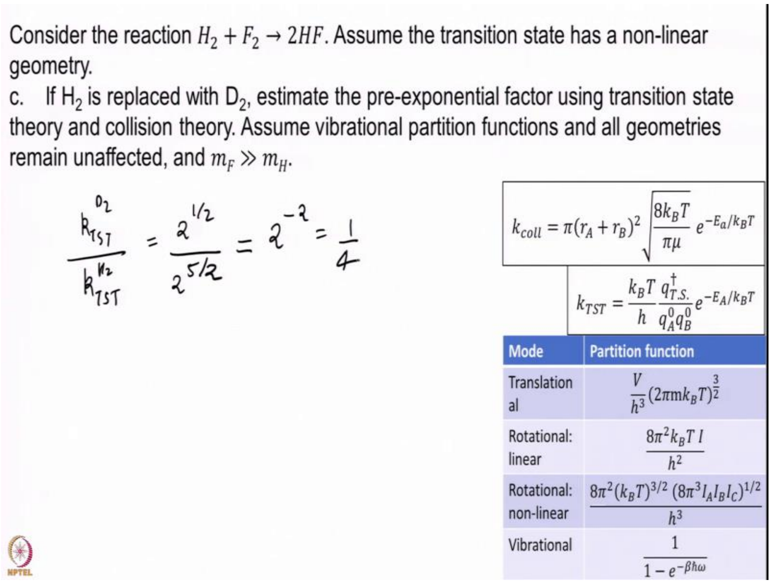


Consider the reaction $H_2 + F_2 \rightarrow 2HF$. Assume the transition state has a non-linear geometry.

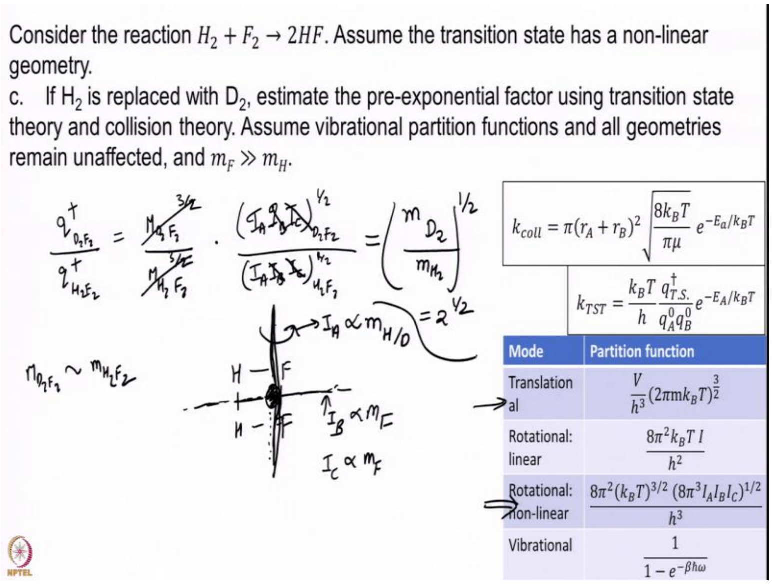
c. If H_2 is replaced with D_2, estimate the pre-exponential factor using transition state theory and collision theory. Assume vibrational partition functions and all geometries remain unaffected, and $m_F \gg m_H$.

$$\frac{k_{TST}^{D_2}}{k_{TST}^{H_2}} = \frac{2^{1/2}}{2^{5/2}} = 2^{-2} = \frac{1}{4}$$

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

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

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



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$$\frac{q^{\dagger}_{D_2F_2}}{q^{\dagger}_{H_2F_2}} = \frac{\cancel{M_{D_2F_2}}^{3/2}}{\cancel{M_{H_2F_2}}^{3/2}} \cdot \frac{(I_A \cancel{I_B} \cancel{I_C})^{1/2}_{D_2F_2}}{(I_A \cancel{I_B} \cancel{I_C})^{1/2}_{H_2F_2}} = \left(\frac{m_{D_2}}{m_{H_2}}\right)^{1/2} = 2^{1/2}$$

$m_{D_2F_2} \sim m_{H_2F_2}$

$I_A \propto m_{H/D}$

$I_B \propto m_F$

$I_C \propto m_F$

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

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So, what have we got in total? This will be, in the numerator I have the ratio of transition state. So, let me just write this as 2 to the power of half. So, this becomes equal to 2 to the power half divided by 2 to the power of 5 over 2, which is what we had shown for the reactants. So, this will be equal to 2 to the power of minus 2 or 1 over 4. So, you can compare it against the collision theory which was 1 over root 2. So again, collision theory and transition state theory will give you qualitatively different results. The ratio is very, very different.

So, we will stop here and in the next module we will solve a few more problems. Thank you very much.