Chemical Kinetics and Transition State Theory
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Lecture 46
Problem solving session 6

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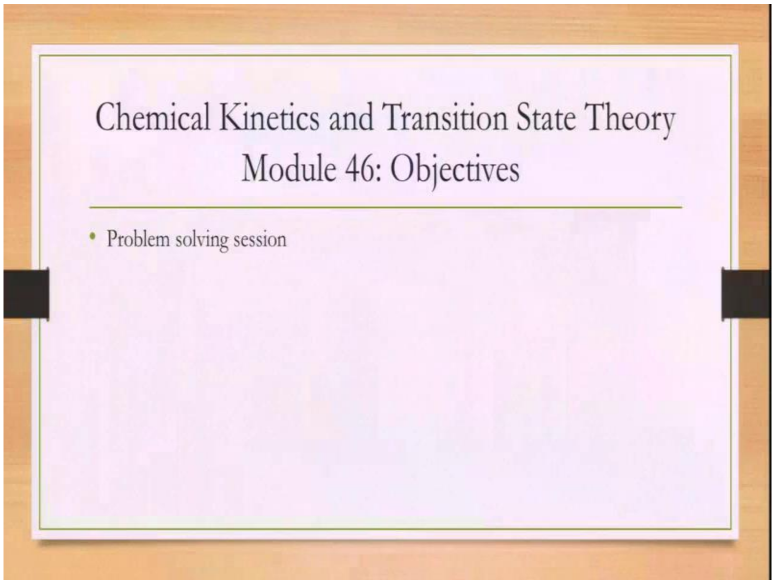

Chemical Kinetics and Transition State Theory
Module 46: Objectives

- Problem solving session

Hello, and welcome to module 46 of Chemical Kinetics and Transition State Theory. So, we will spend a little bit of time today on solving some of the problems with respect to RRK and RRKM theory today. So, let us get right to it.

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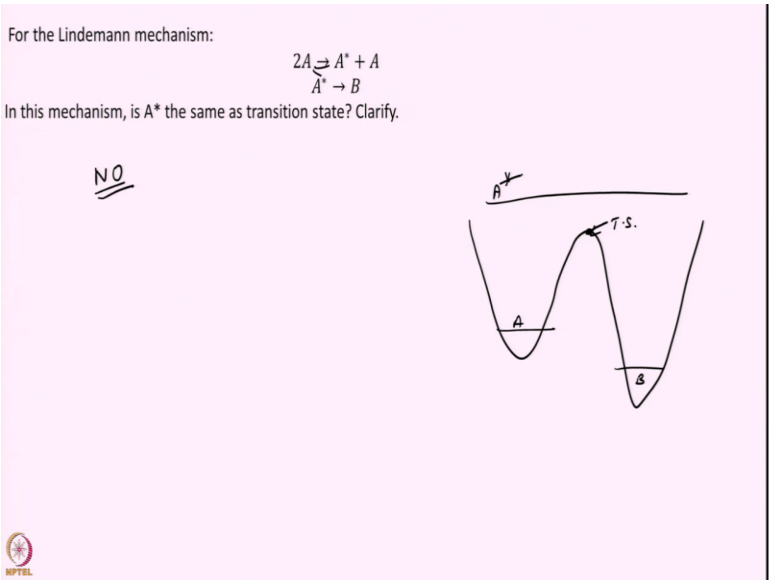

For the Lindemann mechanism:

$$2A \rightleftharpoons A^* + A$$
$$A^* \rightarrow B$$

In this mechanism, is A* the same as transition state? Clarify.

NO

The first problem that I have put forward is for this Lindemann mechanism that we have been discussing, for unimolecular decay this is a back reaction as well, what exactly is A star? Is A star the same as transition state or not? So, take a moment. Think about it. And answer what you think is the right answer. So, hope, you have paused the video and you have answer for yourself yes or no with a clarification.

The correct answer is no. A star is not the transition state. Transition state is a very specific structure. It is the maximum structure along the reaction coordinate and the minimum structure along all coordinates perpendicular to the reaction coordinate. A star does not need to satisfy all these criteria. So, if I again draw this kind of energy surfaces, 1D energy surfaces. This here is A. This here is B. This point is the transition state. But A star is any structure that is above the energy of transition state and it can actually have the same coordinates as the reactant coordinate just with a higher energy. So, A star is not the transition state.

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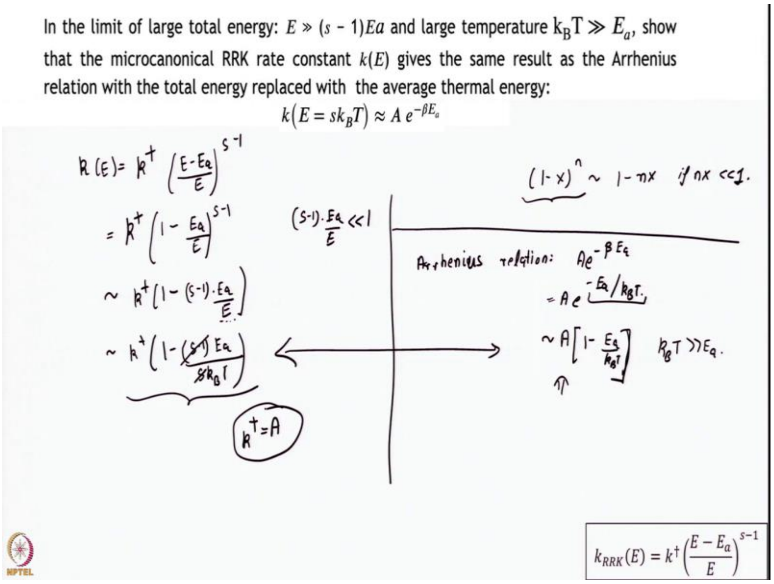

In the limit of large total energy: $E \gg (s-1)Ea$ and large temperature $k_B T \gg E_a$, show that the microcanonical RRK rate constant $k(E)$ gives the same result as the Arrhenius relation with the total energy replaced with the average thermal energy:

$$k(E = sk_BT) \approx A\, e^{-\beta E_a}$$

$$k(E) = k^{+}\left(\frac{E-E_a}{E}\right)^{s-1}$$

$$= k^{+}\left(1-\frac{E_a}{E}\right)^{s-1} \qquad (s-1)\cdot\frac{E_a}{E} \ll 1$$

$$\sim k^{+}\left(1-(s-1)\cdot\frac{E_a}{E}\right)$$

$$\sim \underbrace{k^{+}\left(1-\frac{\cancel{(s-1)}\,E_a}{\cancel{s}k_BT}\right)}$$

$$\boxed{k^{+}=A}$$

$$\underbrace{(1-x)}^{n} \sim 1-nx \quad \text{if } nx \ll 1.$$

Arrhenius relation: $Ae^{-\beta E_a}$

$$= A e^{\underbrace{-E_a/k_BT,}}$$

$$\sim A\left[1-\frac{E_a}{k_BT}\right] \qquad k_BT \gg E_a.$$

$$k_{RRK}(E) = k^{\dagger}\left(\frac{E-E_a}{E}\right)^{s-1}$$

Let us look at the next question. This is a more mathematical question. So, we have looked at the RRK rate at constant energy and the microcanonical RRK rate. How is that rate related to the Arrhenius rate? There has to be some relation. Specifically, when the energy is large, so when I give you this condition that the energy is much, much greater than s minus 1 into Ea, and the activation energy is also large, much greater than kT, then can you work out a relation between this RRK rate compared to the Arrhenius rate and identify what this A is going to come out?

So again, take a pause. This is a slightly harder question. This kind of maths we have not usually worked out in this course. But it is still an important conceptual question. How are, how is microcanonical rate related to canonical rate. So, take a pause, work out to the best of your capability on how to even approach this problem, and then we will discuss it together.

So, hopefully, you have taken a pause. This is a very important concept. How to go between microcanonical and canonical rate constant and you have worked out a solution for yourself. Let us try to work this out together now. So, k RRK at a constant energy is given by this formula, where k dagger is a constant. So, let us first do our mathematics and then we can analyze it what it means.

This is k dagger. Let me write this as 1 minus Ea over E to the power of s minus 1. Now I will use a relation that is the relation that we have not used very often in this course is approximately equal to 1 minus nx, if nx is much, much less than 1. So, this really comes from Taylor expansion. You can think of this and open this whole fact, this power series. So, the higher orders that you will get in x square and x cube that I can ignore if nx is much, much less than 1. That is all I am saying.

So, here you see that we have given this relation to you here. So, what we have is that s minus 1 into Ea over E is much, much less than 1. So, I can approximate this as k dagger into 1 minus s minus 1 into Ea over E. Now, the energy I am replacing with the thermal energy. Where does this thermal energy come from? So, I am assuming I have a lot of energy with me.

I have a big system with me with a lot of energy in it with a lot of oscillators. If that is the case, on average, each oscillator will have kT of energy. That is what actually thermodynamics gives you. Again, something we have not shown in this course, but you can get to your thermodynamics course and show that very easily. This is called equipartition theorem that each harmonic oscillator gets a kT of energy.

I have s harmonic oscillators. So, I have roughly skT of energy. So, here we are talking of large numbers anyway. So, I am going to cancel s and s minus 1. s is some large number. We have a lot of oscillators with us. So, they are approximately equal. So, I get something like 1 minus E over kT. But you notice what is in the Arrhenius relation. Arrhenius relation, let me get to Arrhenius relation here, this is A into e to the power of minus beta Ea. Let me just write it more clearly in terms of kT, but we also have given that the activation energy is also much larger than kT. So, I can approximate this as A into 1 minus Ea over kT, which you see is very similar to what we have here.

So, this is in the limit when kT is much, much greater than Ea. So, this number is small. I can do a Taylor expansion again and show this result. So, you see these results are similar with the identification that k dagger is A. So, when you have a lot of energy, when you have a large temperature, what you will get is essentially the canonical rate constant out from microcanonical rate constant. This is the basic analysis that we are doing here.

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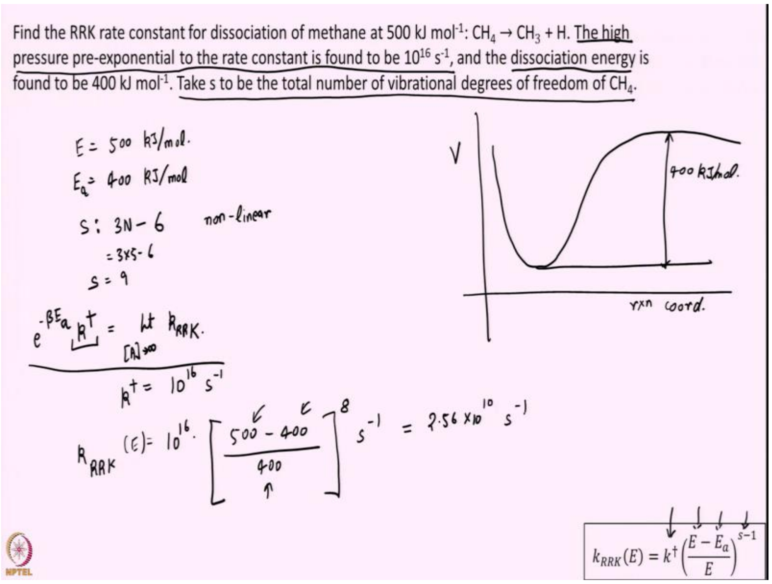

Find the RRK rate constant for dissociation of methane at 500 kJ mol^{-1}: $CH_4 \rightarrow CH_3 + H$. The high pressure pre-exponential to the rate constant is found to be 10^{16} s^{-1}, and the dissociation energy is found to be 400 kJ mol^{-1}. Take s to be the total number of vibrational degrees of freedom of CH_4.

$E = 500$ kJ/mol.

$E_a = 400$ kJ/mol

$s : 3N - 6$ non-linear

$= 3 \times 5 - 6$

$s = 9$

$$e^{-\beta E_a} \underbrace{k^{\dagger}} = \underset{[A]\to\infty}{lt}\ k_{RRK}.$$

$$k^{\dagger} = 10^{16}\ s^{-1}$$

$$k_{RRK}(E) = 10^{16} \cdot \left[\frac{\overset{\swarrow}{500} - \overset{\swarrow}{400}}{\underset{\uparrow}{400}}\right]^{8} s^{-1} = 2.56 \times 10^{10}\ s^{-1}$$

$$\boxed{k_{RRK}(E) = k^{\dagger}\left(\frac{E - E_a}{E}\right)^{s-1}}$$

Let us move to the next question. So, this is a more numerical question now. And these are the kind of questions you should be able to do with the formulas and development that we have done throughout this course. This is a very normal question. For a given reaction at a given energy you have to find the RRK rate constant. And of course, you know the formula.

So, the trick is to finding k dagger correctly, you have to identify all the parameters of RRK. What do you put for k dagger, E, Ea and s. So, take a moment, pause the video and get a number out, final number out with proper units. These are the kinds of questions you will see in your assignments and exams. So, you should be able to do this question. So, take a pause.

Hopefully, you have taken a pause. So, let us work out these numbers now. So, we have to basically identify each of these numbers. E is easy, is 500 kilojoules per mole. Ea is easy that is 400 kilojoules per mole. This is the dissociation energy. Remember that the reaction that we are studying looks, will look something like this along some kind of reaction coordinate and this energy is 400. And so, this is effectively your activation energy. This is the minimum energy you require for the bond to break. So, you will take that.

Let us look at s. So, we are taking s to be the total number of vibrational degrees of CH4. Vibrational degrees of freedom is 3N minus 6 for a non-linear molecule, methane of course is non-linear. Here N is the total number of atoms which is equal to 5 for methane, 4 hydrogen plus 1 carbon. So, we have s as well. I must add a comment for the sake of problem we have taken s to be this total number of vibrational degrees of freedom, but that is not always the case for a good experimental answer.

s usually is smaller than the total vibrational degrees of freedom if you want to match experimental data and that we have discussed a little bit in our previous modules. s is somewhat adhoc in RRK theory and that is a limitation of RRK theory itself. How to get s is not very clear. So, this is just a starting point. Let us take s to be that maximum number of vibrational coordinates.

The final number is k dagger. Now, if you remember we discussed how we calculate k dagger. This k dagger is nothing but the limit of A going to finite of your k RRK into e to the power of minus beta Ea. So, this you can go back and this is the way we calculate k dagger, one of the ways we calculate k daggers. And what we have given is that the higher-pressure pre-exponential to the rate constant is this. K dagger is pre-exponential to the rate constant. So, k dagger is then 10 to the power of 16 second inverse.

So, finally, we put it all together is 10 to the power of 16 into 500 minus 400 divided by 400. Here note that the units will cancel. This is in kilojoules per mole, this is in kilojoules per mole and this is also in kilojoules per mole. So, both numerator and denominator are in kilojoules per mole. So, my units are cancelling.

That is why I am not doing any conversion of units here. To the power of s minus 1, which is 8. After that, you can simply plug it on a calculator and calculate this number out. And that number I calculated and I got 2.56 into 10 to the power of 10 second inverse. So, that is the RRK estimate for the rate constant at 500 kilojoules per mole.

The final problems I want to discuss are much more application based. For the perspectives of exams, these problems I can only give in part. But if you are a researcher, who actually wants to understand how to calculate rate constants for real problems, then you should pay focus. Because when you are doing research you will get problems which do not have a clear-cut analytical answer and you have to make assumptions and estimates in between, and that is the art of science. So, take a little moment. We are here doing a very, very famous problem.

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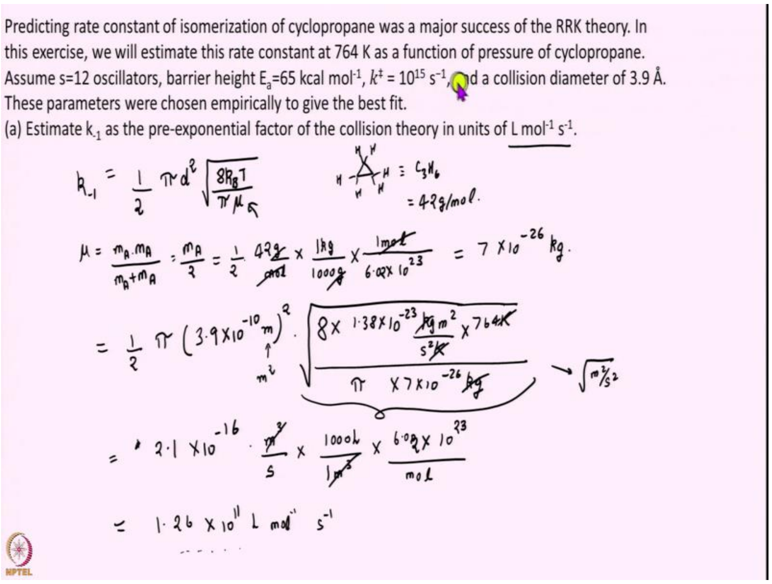

Predicting rate constant of isomerization of cyclopropane was a major success of the RRK theory. In this exercise, we will estimate this rate constant at 764 K as a function of pressure of cyclopropane. Assume s=12 oscillators, barrier height E_a=65 kcal mol^{-1}, $k^{\ddagger} = 10^{15}\ s^{-1}$, and a collision diameter of 3.9 Å. These parameters were chosen empirically to give the best fit.

(a) Estimate k_{-1} as the pre-exponential factor of the collision theory in units of $\underline{L\ mol^{-1}\ s^{-1}}$.

$$k_{-1} = \frac{1}{2}\pi d^2 \sqrt{\frac{8k_BT}{\pi\mu}}$$

$$= C_3H_6 = 42\,g/mol.$$

$$\mu = \frac{m_A \cdot m_A}{m_A + m_A} = \frac{m_A}{2} = \frac{1}{2}\,\frac{42\cancel{g}}{\cancel{mol}} \times \frac{1kg}{1000\cancel{g}} \times \frac{1\cancel{mol}}{6.02\times10^{23}} = 7\times10^{-26}\,kg.$$

$$= \frac{1}{2}\pi\left(3.9\times10^{-10}\underset{\overset{\uparrow}{m^2}}{m}\right)^2 \cdot \underbrace{\sqrt{\frac{8\times 1.38\times10^{-23}\frac{\cancel{kg}\,m^2}{s^2\cancel{K}}\times 764\cancel{K}}{\pi\times 7\times10^{-26}\cancel{kg}}}} \rightarrow \sqrt{m^2/s^2}$$

$$= 2.1\times10^{-16}\cdot\frac{\cancel{m^3}}{s}\times\frac{1000L}{1\cancel{m^3}}\times\frac{6.02\times10^{23}}{mol}$$

$$\simeq 1.26\times10^{11}\ L\ mol^{-1}\ s^{-1}$$

This is the claim of fame for RRK theory calculating rate constant for isomerization of cyclopropane as a function of pressure of cyclopropane. This was a major hurdle in early 1910s and ‘20s and RRK theory had the major breakthrough in getting it exactly right. So, I have provided you a little bit of parameters that people worked out over very tedious work over a decade of work.

So, for this problem, we are looking at 764 kelvin at which the experiment was done. We will assume s equal to 12. Let us just discuss s equal to 12. We have cyclopropane. Cyclopropane has how many atoms? It has 3 carbons and 6 hydrogens, that is a total of 9 atoms. So, 3 and minus 6 the total vibrational coordinates is much more than 12. You can work it out. That is 3 into 9 minus 6, which is equal to how much? It is I think equal to 19 or 18 I think, my bad. You can work it out. It is much more than 12.

But if you choose that higher number, you simply do not get the right experimental answer. So, s equal to 12 is really chosen to get the right answer and that is of course a limitation of RRK theory. If you want to improve it, then we do a RRKM theory. But now let us look at how RRK does it. What is the way of doing RRK? And s is a parameter we fit.

One thing I should point out, we use the same set of parameters for all pressures. What we will not do is for a different pressure we choose a different test that is cheating. We have calculated this s for all values of pressures. So, there is some decency. There is some confidence we have in the model that for this parameter we get it for all possible pressures you can calculate and all possible temperatures. Even as a function of temperature, we are not going to vary s.

Barrier height is of course a fixed number. That is not fitted to anything. K dagger you can calculate as in the last calculation we did for high pressure that is coming from experiment and collision diameter is actually also done as a best fit for all pressures and all temperatures one consonant number and this happens to be the number that gives you the best fit. So, both collision diameter and s are best fit parameters, nothing more can be done about them in RRK theory.

So, we will start out by first calculating k minus 1 in our RRK theory as the pre-exponential factor in units of liter mole inverse second inverse. So, take a pause, get your pens out, get your papers out and do this maths. It is extremely important for the purposes of this course. This k minus 1 you will see as exam questions. The next thing we will discuss is harder to put it in exam, but this k minus 1 by now you should be able to calculate precisely in terms of a number in a given units. So, take a pause, do this calculation.

So, hopefully, you have taken a pause. It is extremely important that you should be able to do this calculation now. But let us do it together now. So, k minus 1, from collision theory here I have not even provided you the formula this time. You should be able to go ahead, look back into your notes, go back to your modules, go on the Internet, whatever you need to do and get this formula, what the correct formula you should use. Here k minus 1 is used for an atom colliding with itself. Remember, for that, we used a slightly different formula. When we have A plus A we have a factor of half. Do not forget this factor.

Once we have the formula, all that matters is plugging in the numbers correctly in proper units that takes time. Without practicing you will not be able to get the units right. I can promise you. The first time you do it, you will do mistakes. So, do not make your first attempt in the exam directly. You must do these calculations on your own. So, let us look at all the different parameters. First, let us look at mu. So, this is the reduced mass mA into mA. I have only one molecule. So, this is equal to mA over 2, where this is mass of cyclopropane.

Now, cyclopropane is what, this molecule with each carbon having 2 hydrogens. So, this is C_3H_6. So, the mass is carbon is 12, hydrogen is 1. So, 12 into 3 is 36 plus 6 is 42 grams per mole. But what is the unit I want mu in. I have to put mu here. I want it in kilograms, not grams per mole.

So, I have to be careful with that. Let us change our units half into 42 grams per mole. We did these calculations a lot when we were discussing collision theory. So, if you are confused, you can go back. 1 kilogram and 1000 grams. Also remember to convert moles into atoms, we have to use Avogadro number here. So, this you can plug in and I got 7.

So, remaining let us plug it in. I have half pi d is given to be 3.9 angstroms, angstrom is 10 to the power of minus 10 meters square, kB is 1.38 into 10 to the power of minus 23-kilogram meter square per second square kelvin. Remember your units. Temperature is 764 kelvin pi and mu we just calculated. Kelvin cancels with kelvin, kilogram cancels with kilogram. So, if I plug all of these numbers in, right now, it is just a matter of simply punching it into a calculator.

Now, what is the current unit? If I look here, I will get meter square from here. From the square root, I will get root of meter square per second square which is nothing but meter per second. So, if I multiply them together, I get meter cube per second, not the units I want it in. So, I do 1000 liter in 1 meter cube into, I finally want, put in the Avogadro number 6.02 into 10 to the power of 23 per mole. So, this I will get in liter mole inverse second inverse. So, once I punch these numbers in, I get.

And again, a sanity check, you see that order of magnitude is more or less right. What we did before you get usually 10 to the power of 9 to 10, but also see that the temperature is very hot right now at 764. Earlier we were looking at room temperature. So, it is natural that we have gotten a slightly higher number, reasonable enough and the d is also large. Cyclopropane is a big molecule. So, we have a large 4 angstrom diameter.

I mean, it is not that we are getting 10 to the power of 20 or 10 to the power of 2. So, that sanity check you should always do once you get the final number. You should have a sense of what these numbers look like. And by the way, these are, I mean, I am not making up these numbers. These calculations were done in ‘20s and ‘30s. And these are the results they had actually got. So, these parameters that I am putting here are actually from papers. I am not making up these numbers.

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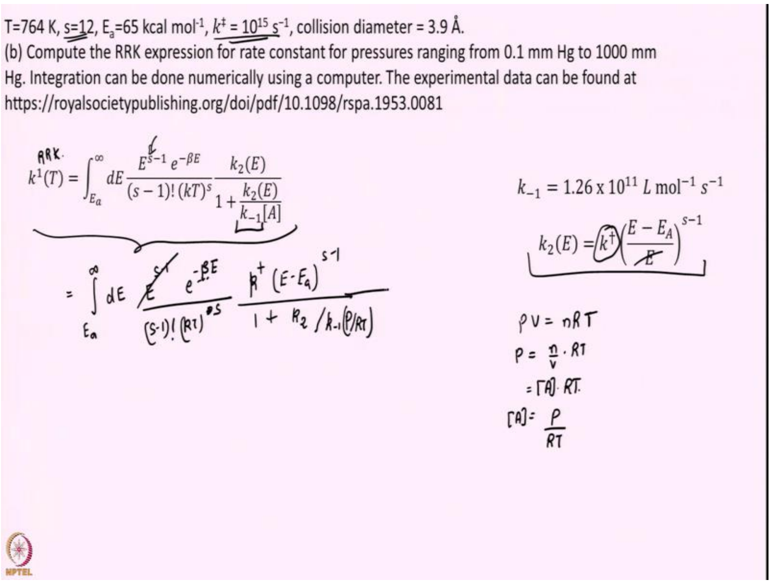

T=764 K, s=12, E_a=65 kcal mol^{-1}, $k^{\ddagger} = 10^{15}\ s^{-1}$, collision diameter = 3.9 Å.

(b) Compute the RRK expression for rate constant for pressures ranging from 0.1 mm Hg to 1000 mm Hg. Integration can be done numerically using a computer. The experimental data can be found at https://royalsocietypublishing.org/doi/pdf/10.1098/rspa.1953.0081

RRK.

$$\underbrace{k^1(T) = \int_{E_a}^{\infty} dE \frac{E^{s-1} e^{-\beta E}}{(s-1)!\,(kT)^s} \frac{k_2(E)}{1 + \frac{k_2(E)}{k_{-1}[A]}}}$$

$$= \int_{E_a}^{\infty} dE \frac{\cancel{E^{s-1}}\, e^{-\beta E}}{(s-1)!\,(RT)^{s}} \frac{k^{\dagger} (E-E_a)^{s-1}}{1 + k_2 / k_{-1}(P/RT)}$$

$$k_{-1} = 1.26 \times 10^{11}\ L\ mol^{-1}\ s^{-1}$$

$$\underbrace{k_2(E) = \boxed{k^{\dagger}} \left(\frac{E - E_A}{\cancel{E}}\right)^{s-1}}$$

$PV = nRT$

$P = \frac{n}{V} \cdot RT$

$= [A] \cdot RT$

$[A] = \frac{P}{RT}$

You can find these parameters actually in this paper. In this, this is a paper in ‘50s. But this paper is actually taking parameters from older papers and tabulating up the data. So, you can look at this paper. It is very well written. That is a reason I have cited this one. And it gives a very nice overview on how this RRK calculation was done and how it successes, how its success was.

So, now let us do the final thing. We are not interested really in k minus 1, we are interested in the final RRK rate and the rate of cyclopropane isomerizing. And this is the formula we had derived for RRKM at the end of the day. You can go back into the module and look at it. We have gotten k minus 1 only so far one parameter. s was chosen to be 12. This we already know.

What about k2? k2 is this. For this, k dagger is already calculated and I have given it to you. Again, the way to calculate it is another problem we discussed in the last problem. You look at the infinite pressure result and from that you extract the pre-exponential factor. So, that is the way of calculating k dagger.

So, what remains? We have everything here. So, we basically plug these numbers in into this exponential, E to the power of s minus 1, let me just write this one, beta also you know as temperature. K2, let me just plug in the numerator. One term actually cancels out. So, that is the reason I am putting it in. And you notice, I have a denominator e to the power of s minus 1. So, this time will cancel out. So, this thing will cancel out. So, I am not writing that. A here, you cannot do much better.

How do I get concentration of A? See experimentally, they are not monitoring concentration at all. They are monitoring pressure. That is the way experimentalists behave. You are a theoretician, you have, they have the experimental data with them. And they have came to you and asked whether you can fit it or not. So, what we will do and this is basically a rough estimate. We will use ideal gas law. And that is what you have to do as a theoretician. You have to make reasonable approximations.

So, pressure is n over V into RT, which is nothing but concentration of A into RT. So, concentration of A is nothing but P over RT. So, instead of this concentration of A in my formula, I will write P over RT. I have a lot of fractions, but hopefully it makes sense. At the end of the day, you have to be careful. We have reached this point. Now, what? This integration actually cannot be done analytically. It is not possible.

So, now we take help from a computer. Again, that is the reason it is beyond the full purview of this course, because we are not telling you how to do, be able to do these integrals numerically. What I did is to write a little Fortran code for myself and I will share this Fortran code with you. This we will upload as a file.

But I know many of you are much smarter than me. Fortran is perhaps an outdated language. You can write your own Python code. You can write your own Mathematica code or MATLAB code or you can go to the Internet and Internet now provides these. You can put the put an integral and do the calculation. So, you can do that as well.

So, you do it however you want. In fact, I encourage you to do it your way and email me your program. You do it by Mathematica, MATLAB, Python, whatever way and teach me, because I do not know how to do that actually. So, right now, it is your turn to become the teacher and me to become the student and show me how it is done beyond Fortran, whatever way is your favorite way to do this integral.

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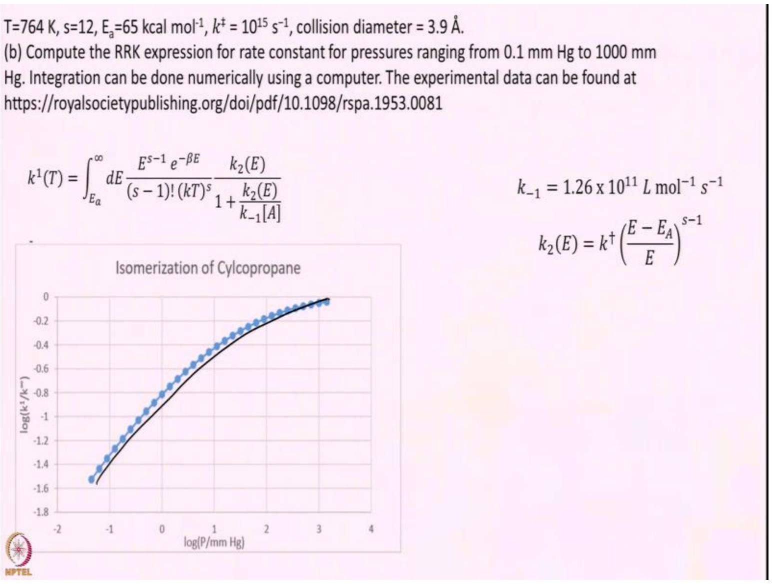

T=764 K, s=12, E_a=65 kcal mol^{-1}, $k^{‡} = 10^{15}$ s^{-1}, collision diameter = 3.9 Å.

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$$k^1(T) = \int_{E_a}^{\infty} dE \frac{E^{s-1}\, e^{-\beta E}}{(s-1)!\,(kT)^s} \frac{k_2(E)}{1 + \frac{k_2(E)}{k_{-1}[A]}}$$

$$k_{-1} = 1.26 \text{ x } 10^{11}\ L\ \text{mol}^{-1}\ s^{-1}$$

$$k_2(E) = k^{\dagger}\left(\frac{E - E_A}{E}\right)^{s-1}$$

Isomerization of Cylcopropane

And once that integral was done, I got the following result. You do it yourself. And this is proper research now. We had started with a particular reaction. The s, now when you have a code, you can actually vary this s and collision diameter. There is no reason to believe s to be the following and a collision diameter to be the following. Actually, the result that you get out here matches extremely well to the experiment. I am not even drawn experimental result for that reason. But you can see how the result varies with s that is the homework for you. How the result varies with collision diameter.

The fall, this result was obtained for that, I mean, so that we get this result for this, you can take this to be the experimental answer basically and it turns out for this particular collision diameter and s you will get this particular graph. So, now the ball is in your court. You can toggle your parameters and see what you get.

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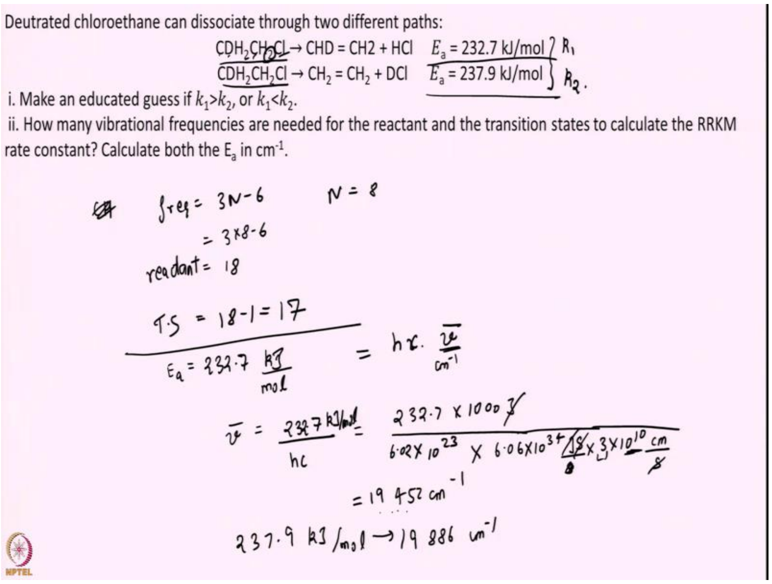

Deutrated chloroethane can dissociate through two different paths:

$CDH_2CH_2Cl \rightarrow CHD = CH2 + HCl$ $E_a = 232.7$ kJ/mol R_1

$CDH_2CH_2Cl \rightarrow CH_2 = CH_2 + DCl$ $E_a = 237.9$ kJ/mol R_2.

i. Make an educated guess if $k_1 > k_2$, or $k_1 < k_2$.

ii. How many vibrational frequencies are needed for the reactant and the transition states to calculate the RRKM rate constant? Calculate both the E_a in cm^{-1}.

$freq = 3N-6$ $N = 8$

$= 3 \times 8 - 6$

readant = 18

$T.S = 18 - 1 = 17$

$E_a = 232.7 \frac{kJ}{mol} = hc. \underset{cm^{-1}}{\bar{\nu}}$

$\bar{\nu} = \frac{232.7\ kJ/mol}{hc} = \frac{232.7 \times 1000\ J}{6.02 \times 10^{23} \times 6.06 \times 10^{34}\ Js \times 3 \times 10^{10}\ \frac{cm}{s}}$

$= 19\ 452\ cm^{-1}$

$237.9\ kJ/mol \rightarrow 19\ 886\ cm^{-1}$

We will end with one final problem. This again is meant more for people who are doing research and get the actual numbers out one way or another. You are free to make reasonable approximations. So, let us look at an organic reaction. And what I want to emphasize is from this course is have you actually gained anything.

So, let us look at this reaction. You have this D as an isotope of hydrogen. And you can have two possible reactions either HCl can dissociate out or DCl can dissociate out. So, you organic chemists can work out right possible mechanisms, draw arrows and all that. And here is my gauntlet to the organic chemists here is my audience.

I have given you the activation energy. How will you predict which goes faster? Well, of course, you organic chemists will tell me that they can do the experiment and figure it out. That is one way of doing it. I am asking, can I also predict it mathematically? Is there a reason I can give which is faster? And at the end of this course, you should be in a position to do it.

So, I want you to, if you can make an educated guess, guess whether k1 is greater than, so this rate constant, let us say is k1 and this rate constant is k2, can you make an educated guess? Use your intuition and tell me which is faster? I am not going to answer that. That is on you. You make an answer and you email me what you get, what you think and what is your reasoning. This is an open ended question. This does not have a right or wrong answer.

What I will do is make, use our theories now and calculate this rate. So, we know that RRKM is a better theory than RRK theory. So, we will use the RRKM theory and calculate these rates now. And we will see what we get. And I will solve it only partially. This is the end of the course. You all should be able to do this kind of calculations and make your own estimates. So, you should not become dependent on been given, been spoon feed on everything.

So, the first question I will ask you is, what are the parameters you need if you are doing RRKM theory? Well, you need frequencies. So, for now at least for this discussion, I will limit only to frequencies and not rotations, but you should. I am limiting, but you should not be limited. You should try to think how will you include rotations as well in your calculation.

So, my first question to you is, well, how many frequencies do you need? So, let us say you have a theoretical friend with you, whom you can go, who will do the electronic structure calculation, how many frequencies you expect your theoretician friend to give you? He is going to give you some numbers. You have to cross check whether your theoretical friend is doing the right job or not, maybe he is making mistakes, maybe he is fooling you. It is your research. You have to get it right. So, you make an estimate on the number of vibrational frequencies you need for the reaction and transition state. Take a pause and calculate it.

Hopefully, you have done a calculation. This is not a hard calculation. So, I will, it is essentially counting the number of atoms. Frequencies equal to 3N minus 6. Here n is 1, 2, 3, 4, 5, 6, 7, 8. And it is of course a non-linear molecule. So, 3 into 8 minus 6 is 18. This is for reactant. Remember, transition state will have one frequency less.

Now, your theoretician friend will actually give you frequencies in wave numbers. Any electronic structure package gives out number in wave numbers. It is your job now to figure out these activation energy therefore in wave numbers. Once you are doing these calculations, you will need to do these answers in wave numbers then. So, that is your next job. Take a pause and calculate convert both of these activation energies in wave numbers.

So, hopefully, you have taken a pause and actually done this. If you do not do it on your own and only listen to me, once you start doing it on your own, once you get a problem like this, you will not be able to do it, I guarantee you unless you try it on once on your own. So, this is a golden opportunity for you. I am also going to solve it and then you can match whether I have done it correctly or not.

So, Ea equal to let us say 232.7 kilojoules per mole. How do I go to wave numbers? This is equal to hc into nu bar, where nu bar is in wave numbers. That is how I convert. So, nu bar is 232.7 divided by hc. So, I have to be very careful of units. So, I will write this as 232.7 into 1000 joules divided by 6.02 into 10 to the power of 23 for converting moles. So, I have a number in joules, h I write as this, c I write as. Remember, I am not writing in meters per second because I want the answer in centimeter inverse. That is why it is 10 to the power of 10. Be very careful with your units.

This is supposed to be joules into seconds, my mistake there, joules cancels with joules, seconds cancel with second. And if I plug it in, I will get 19452-centimeter inverse. So, you can cross check your calculation. If you do not plug in the exact numbers, here actually I get this with putting in exact value of c, not 3, but 2.998 whatever it is. So, you might get a number that is slightly off here and there, but close by. For 237 the other one, I get 19886 wave numbers.

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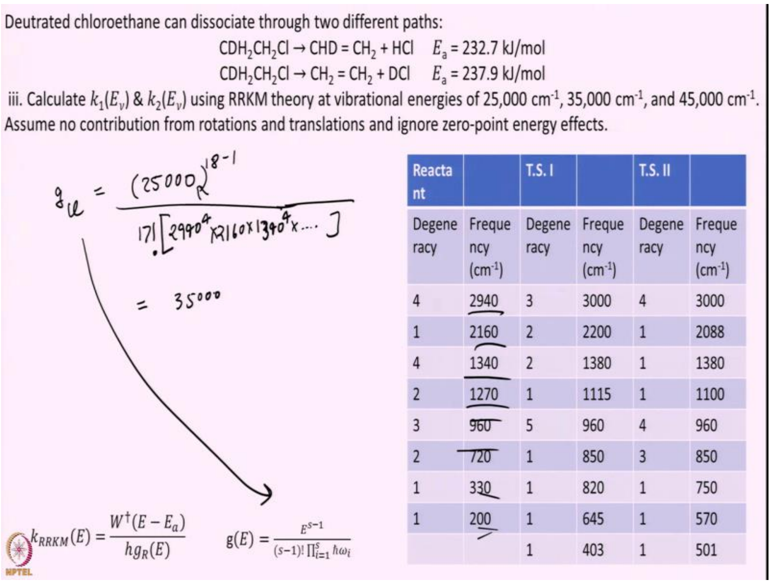

Deutrated chloroethane can dissociate through two different paths:

$CDH_2CH_2Cl \rightarrow CHD = CH_2 + HCl \quad E_a = 232.7$ kJ/mol

$CDH_2CH_2Cl \rightarrow CH_2 = CH_2 + DCl \quad E_a = 237.9$ kJ/mol

iii. Calculate $k_1(E_v)$ & $k_2(E_v)$ using RRKM theory at vibrational energies of 25,000 cm^{-1}, 35,000 cm^{-1}, and 45,000 cm^{-1}. Assume no contribution from rotations and translations and ignore zero-point energy effects.

$$g_{ve} = \frac{(25000)^{18-1}}{17!\left[2940^4 \times 2160 \times 1340^4 \times \ldots\right]}$$

$= 35000$

Reactant		T.S. I		T.S. II	
Degeneracy	Frequency (cm^{-1})	Degeneracy	Frequency (cm^{-1})	Degeneracy	Frequency (cm^{-1})
4	2940	3	3000	4	3000
1	2160	2	2200	1	2088
4	1340	2	1380	1	1380
2	1270	1	1115	1	1100
3	960	5	960	4	960
2	720	1	850	3	850
1	330	1	820	1	750
1	200	1	645	1	570
		1	403	1	501

$$k_{RRKM}(E) = \frac{W^{\dagger}(E - E_a)}{hg_R(E)} \qquad g(E) = \frac{E^{s-1}}{(s-1)!\prod_{i=1}^{s} \hbar\omega_i}$$

So, now let us actually calculate these rate constants using RRKM theory. So, your theoretician friend comes in. You ask him, you have asked him to do the calculations and these are the frequencies he has provided you. At the reactant which is this, he has given you all these set of frequencies with degeneracies. So, there are frequencies, multiple frequencies appear with the same value.

So, first thing let us add these numbers together and see if we get 18 or not. 18 is what we had calculated. So, 4 plus 1, 5 plus 4, 9, 11, 14, 15, 16, 17, 18. Your theoretician friend is not completely wrong. He has making some sense. You have two transition states, one for this reaction and one for this reaction. He has done his job and given you these frequencies. Let us add these together and get 17 or not. 3 plus 2, 5, 7, 8, 13, 14, 15, 16, 17, perfect. Let us add these numbers together 4, 5, 6, 7, 3, 10, 14, 15, 16, 17. So, never blindly trust your theoretician friend. That is a bad idea. Make sure these numbers add up together. So, that is fine.

But how do I get these k1 and k2? Your experimental friend has simply given you this big table. What now. So now we will have to, well, RRKM formula is given by this. This we derived. How do I get w and gR? What do we do with them? Here is when we have to use our intuition. First thing note that your, these energies are very large.

So, I have just chosen a few energies above the barrier height. The barrier height is close, a little less than 20,000. So, I have chosen energies above 20,000 and a few sample points. You can calculate more. Why not? What limits you? You can write it, draw it, actually make a plot of k1 and k2 as a function of this energy and then do a thermal average.

So, here I am limited. I am doing you a little bit less for what and you are a researcher. You are free. You are, you have the open sky with you. Fly as high as you want. But how do you get W dagger and gR that is what I am trying to get to here. G I will calculate classically. That is fine, because g is for the reactant at this energy which is much more than kT. So, g it is absolutely fine to use the classical formula.

So, at 25,000 wave numbers, I would write 25,000 to the power of 18 minus 1 divided by 17 factorial into a product of all these frequencies. So, it will be 2940 to the power of 4, because 2940 is appearing 4 times into 2160 into 1340 to the power of 4 into dot, dot, dot. So, I am not going to plug these numbers for you. It is your job. You do it. You do it for different values of this as well. So, I will calculate it at 35,000 as well or whatever energy you are interested in. I have put these energies out of the blue. You choose your energies.

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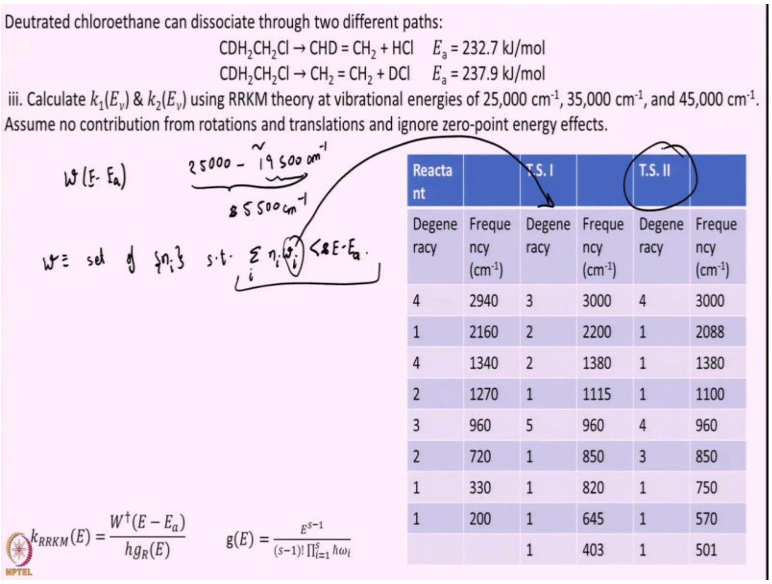

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$W(E-E_a)$

$\underbrace{25000 - \overset{\sim}{19500}\ cm^{-1}}_{8\,5500\ cm^{-1}}$

$W \equiv$ set of $\{n_i\}$ s.t. $\underbrace{\sum_i n_i \omega_i < 8 E - E_a}$.

Reactant		T.S. I		T.S. II	
Degeneracy	Frequency (cm^{-1})	Degeneracy	Frequency (cm^{-1})	Degeneracy	Frequency (cm^{-1})
4	2940	3	3000	4	3000
1	2160	2	2200	1	2088
4	1340	2	1380	1	1380
2	1270	1	1115	1	1100
3	960	5	960	4	960
2	720	1	850	3	850
1	330	1	820	1	750
1	200	1	645	1	570
		1	403	1	501

$$k_{RRKM}(E) = \frac{W^{\dagger}(E - E_a)}{h g_R(E)} \qquad g(E) = \frac{E^{s-1}}{(s-1)! \prod_{i=1}^{s} \hbar\omega_i}$$

Finally, how do I calculate this W? W also have a classical answer. But that is a bad idea, why, because W is calculated at E minus Ea. So, let us look at 25,000 minus Ea for 19,000, roughly 500 wave numbers, let us say, that is roughly my barrier height. So, you see this number is not very large. This number is roughly is how much 5500 wave numbers, much smaller. So, doing much smaller compared to what, compared to your frequencies. Your frequencies are in the order of 2, 3000 numbers here. And this is also in the order of a, I mean, a little bit more. This is not very large.

So, that is the sense you have to get now if you are doing actual research. So, here we have to actually manually calculate W. W set of quanta's ni such that the total energy is less than your E minus Ea. How many possible nis I can construct such that this holds and omega i's for transition state to 1, you will choose this one. And for transition state 2, you will choose this one. So, you will get two different set of Ws for the two different calculations. So, that again I am leaving it to you. You can do it manually or you can write a code. I have written a code for myself in Fortran. I am old fashioned. So, you can write a code in Python perhaps. So that is another exercise for you.

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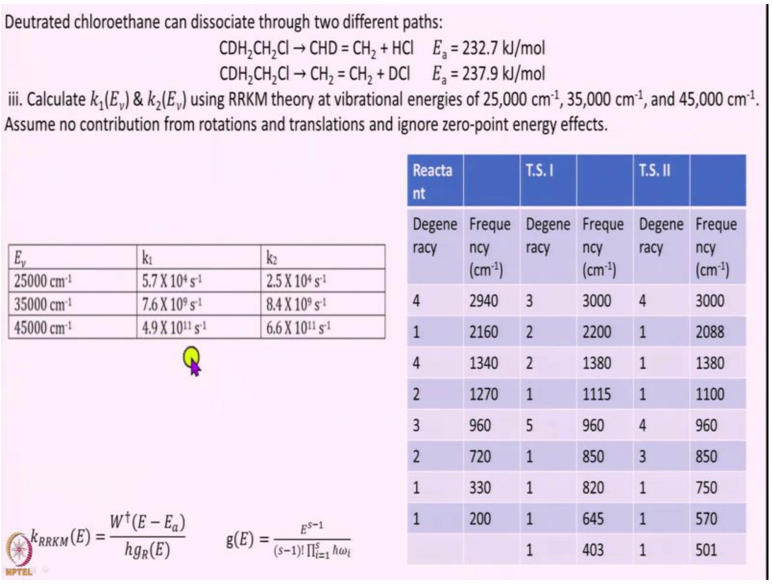

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E_v	k_1	k_2
25000 cm^{-1}	$5.7 \times 10^4 s^{-1}$	$2.5 \times 10^4 s^{-1}$
35000 cm^{-1}	$7.6 \times 10^9 s^{-1}$	$8.4 \times 10^9 s^{-1}$
45000 cm^{-1}	$4.9 \times 10^{11} s^{-1}$	$6.6 \times 10^{11} s^{-1}$

Reactant		T.S. I		T.S. II	
Degeneracy	Frequency (cm^{-1})	Degeneracy	Frequency (cm^{-1})	Degeneracy	Frequency (cm^{-1})
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Finally, these are the numbers I get. So, this is a benchmark for you. You can calculate it for yourself. One thing I just want to point out, the first question I asked whether k1 is greater than k2 or k1 less than k2, there is no clear answer to it actually, the correct answer. At different energies, you will get different answer. At lower energies, you will get k1 is greater than k2. At higher energies, you get k1 less than k2. And you should be able to actually rationalize this.

The point is at smaller energies it is the barrier height that matters. And the barrier height of one is smaller. So, you get that to be a faster rate. But when your energy is large, the small difference is barrier height of 5 kilojoules per mole does not really matter and entropy takes over. And as it turns out, the second one is entropically favored. So, therefore you get a rate of k2 larger than k1. So, that you could have, also have reasoned out using your intuition and now you have the capability to do it.

Here I am not solving the full thing intentionally, because I want you to do it on your own. And I am not putting it as an assignment problem, because it goes a little bit beyond a scope of the course, because you have to write programs to calculate these kinds of things. So, I do not want to do that as an assignment which is graded. But if you are a researcher, you should absolutely attempt this problem and see if your number matches. If they are not matching, email me, maybe I have made a mistake. It is very possible.

So, with that, I will stop. This was a slightly longer module. And this is the end of the course. Now, hopefully, you have gained abilities to be able to calculate rate constants. You can, as you have seen, a little bit of intuition goes in all of this. You should never plug in formulas blindly. You have to think what formulas to use when. When I should I use classical answer? When should I use quantum answer? When is rotation important? Here, by the way, I have not included rotations for example. Of course, they are important. So, you should make an attempt at including them. And once you have included then email me. Let us have a conversation.

So, hopefully, by this course, you have learned how to use transition state theory, RRK theory, RRKM theory and a bit of molecular dynamics of rolling surfaces on these energy surfaces to get rate constants, to get dynamics out. Thank you very much.