Chemical Kinetics and Transition State Theory
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Lecture 44
Unimolecular decay – RRK's approach

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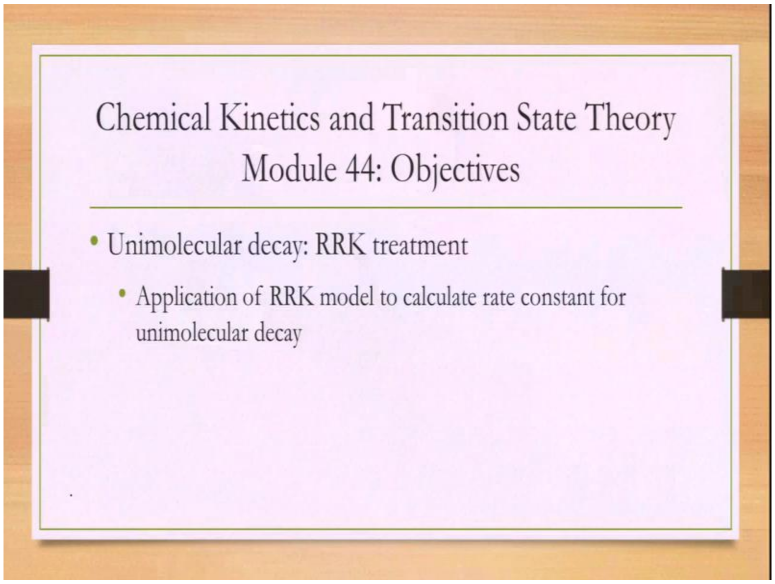

Chemical Kinetics and Transition State Theory
Module 44: Objectives

- Unimolecular decay: RRK treatment
  - Application of RRK model to calculate rate constant for unimolecular decay

Hello, and welcome to module 44 of Chemical Kinetics and Transition State Theory. In the last module, we relooked at unimolecule decay in more detail and we found that there is a little discrepancy if we build a simple model for unimolecular decay that we had looked long time ago and compare it with experimental data. So, today, we are going to look in more detail with a different approach that R, R and K had come up with. R, R and K again are Rice, Ramsperger and Kassel and trying to resolve the differences we get with experiment.

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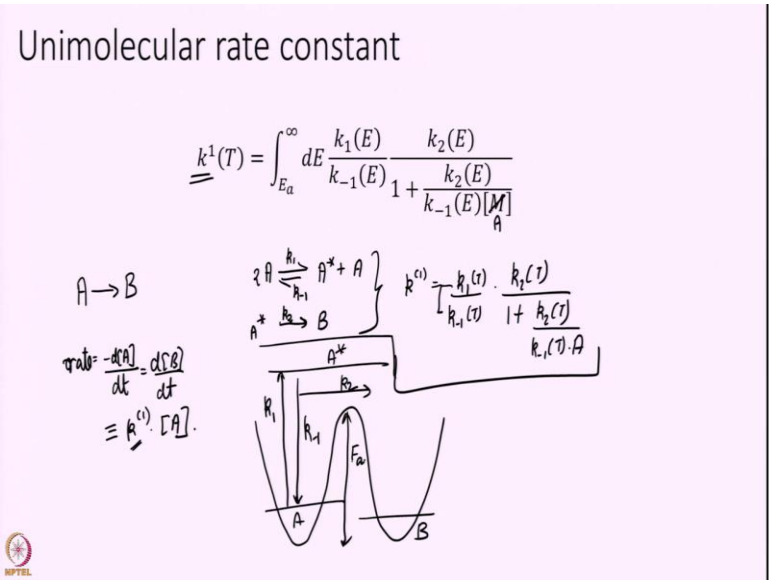

Unimolecular rate constant

$$\underline{\underline{k^1(T)}} = \int_{E_a}^{\infty} dE \frac{k_1(E)}{k_{-1}(E)} \frac{k_2(E)}{1 + \frac{k_2(E)}{k_{-1}(E)[\overset{}{\underset{A}{\cancel{M}}}]}}$$

$A \rightarrow B$

$$2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_2} B$$

$$k^{(1)} = \frac{k_1(T)}{k_{-1}(T)} \cdot \frac{k_2(T)}{1 + \frac{k_2(T)}{k_{-1}(T) \cdot A}}$$

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

$$\equiv k^{(1)} \cdot [A].$$

So, what is, a quick recap of what we had discussed in the last module? What is, again, the problem we have the unimolecule decay, the overall reaction looks like this, some A going to B, only one reactant. And the mechanism of this proposed by Lindemann was as follows. Two molecules of A collide with each other to give an excited A star and A and A star gives B. You can, of course, use chemical kinetics and work out the overall rate constant for this problem. What we, this k1 is defined as rate equal to minus dA over dt equal to dB over dt. And I am defining this rate to be equal to k1 into concentration of A.

So, when I am defining this, I am not assuming this A to going to be B elementary. Therefore, this k of 1 is not a number. It is depends on the concentration of A, fair enough. When I work out the kinetics of this and try to find k1, what you will get is and just we showed a long time ago, k1 over k minus 1 of, these are all functions of temperature, you will get this quantity. I am sorry, this is supposed to be A.

The problem is that this result does not matches well with experiment. There are, it has qualitative agreement, but not exactly agreement. And so, then this new idea came about that here we are assuming this k1, k minus 1 and k2 to be independent of each other. We are calculating them one by one as simple numbers as a, at a given temperature. But that may not be right. Suppose this is A, this is B and this is somewhere A star, k1 is this, k minus 1 is this and this is k2. So in this model, the problem is that this k1 takes me to A star and at that given energy

A star has either a choice to become a product B with rate constant k2 or come down with the rate constant k minus 1.

So, these are not, I cannot calculate them as functions of temperature. I have to look at each energy, what is happening. So instead of writing this, we write it as a function of energy, the same quantity, and integrate over all possible energies above the barrier height. Ea again is this barrier height. Below, if E is less than Ea, we know that more reaction will happen. So we integrate over all energies more than this barrier height.

So, now the question becomes, how do I calculate k1, k minus 1 and k2? So R, R and K, Rice, Ramsperger and Kassel, had given a recipe to calculate this and that is what we will discuss today. So the basic underlying model for this calculation of k1, k minus 1 and k2 has what we have discussed a few modules ago, when we were calculating rate constant at a given energy. Remember, now we are thinking of one given energy calculate this k1, k minus 1 and k2 and then integrate over all energies. So again that picture of constant energy calculation becomes important.

So, the RRK model was that my molecule comprises a bunch of harmonic oscillators and all harmonic oscillators have the same frequency nu. So I have s oscillators with frequency nu and the rate of the reaction is proportional to the probability that mode 1 has energy E greater than Ea.

And I have arbitrarily chosen mode 1 to be the reaction coordinate. You could have chosen mode 7 or mode 9, whatever is your favorite number. 1 is my favorite number. So I decide that mode 1 is a reaction coordinate. So we have discussed this model before and today we will use this model to calculate this unimoleculer decay rate constant.

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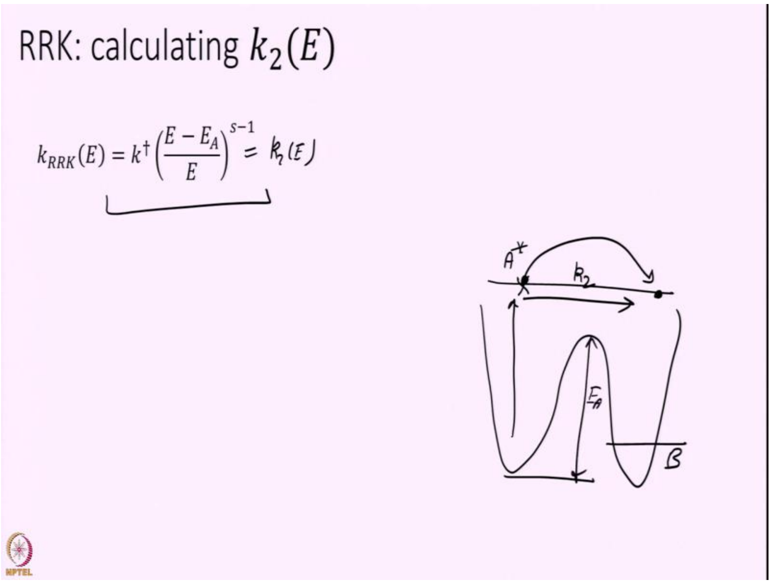

RRK: calculating $k_2(E)$

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

So, the first thing that we have already solved for is the k2 of E. Once more what is k2 of E, if this is A star k2 is that if I have come up here going from A star reactant to B in the product. So, and at that given energy, so going from here to here. So within the RRK model, we had calculated this a few modules ago and we had shown that this is given by this expression. E is of course, a total energy, Ea is again the barrier height and s is a number of oscillators. So one constant down k2 of E.

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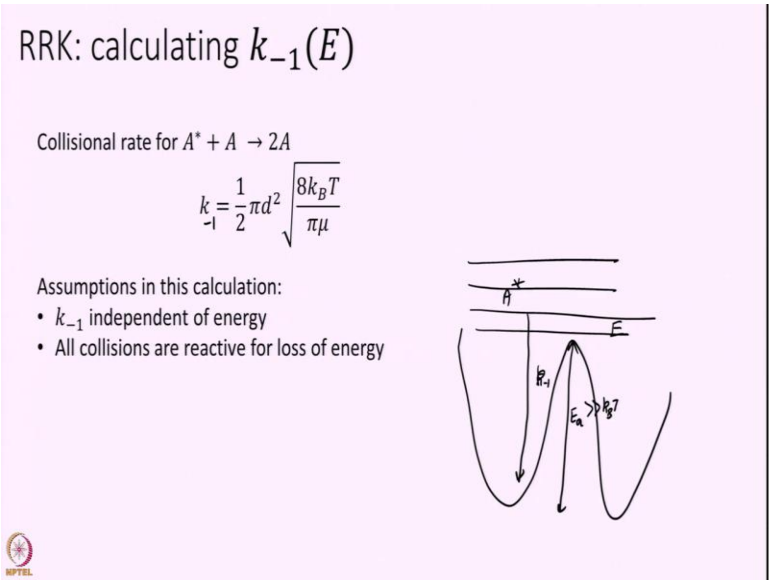

RRK: calculating $k_{-1}(E)$

Collisional rate for $A^* + A \to 2A$

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

Assumptions in this calculation:

- k_{-1} independent of energy
- All collisions are reactive for loss of energy

The second constant k minus 1, k minus 1, the prescription given was and it is going to be a somewhat approximate prescription, we calculate k minus 1 using coalition theory. That is not the big approximation really. I like my 1D surfaces. This is A star at that given energy E. k minus 1 is the rate of losing energy. That is important. It is not gaining energy, but losing. And the mechanism that is being thought of is that this A star is there, zigzagging at very high energy and it collides with some A and loses all of its energy.

So, we know how to calculate that rate constant of collisions and all that using collision theory. And the collision theory of the same atom colliding with itself is given by this expression. This was discussed in great detail. Remember this factor of half comes because same atom is colliding with itself. It is A plus A. It is A star plus A, but A star still has the, is still equivalent to A. D is the diameter of A and mu is the reduced mass.

There are two critical assumptions we make when we have written this. First, you note that this k minus 1, it supposed to be k minus 1 is independent of energy. This might seem like a shocker, because so far we have been arguing that we have to make these k1, k minus 1 and all these as a function of energy and not as a function of temperature. But here I come and I say k minus 1 is a function of temperature alone. It is a gross approximation, agreed.

But if you start thinking about it a little bit more, what we are really saying is, let us assume that this activation energy Ea is large, it is much greater than kt let us say. So this energy is a large number compared to kt. So what it is saying is, if your energy is here or your energy is here or your energy is here, it really does not matter. I have to be, I have to lose energy.

So this k minus 1 dependence on energy will not be very high. The idea I am saying is if you have 1,000 kilojoules per mole of energy, instead of 1,010 kilojoules per mole of energy or 1,100 kilojoules per mole of energy, this k minus 1 is not going to change exponentially with it.

So let us just assume it to be a constant. Well, one question that perhaps you are asking, my energy is going up to infinite. So there should be a difference between 1,000 kilojoules per mole and 5,000 kilojoules per mole, agreed. But also remember that if the energy is much larger than the barrier height, the rate constant will anyway come down a lot and that will come out naturally in this theory. So that is why energies that are way beyond the barrier height do not contribute anything. So we only end up with those energies that are close to barrier height, and in that range, I can assume k minus 1 to be almost a constant.

Second assumption, you will also notice that I have missed the coalition factor here that when I was discussing the collision theory, I said is a very, very important, without that the rate constant will be completely wrong and you will get a 0 mark if you do not include that. But here I come and I have happily forgotten to write that for a good reason.

The reason is that I am losing energy here, not gaining energy. When you have already very high energy and if you hit another molecule, the probability is fairly high that you will just lose that energy. As opposed to if you have two molecules that are moving slower and they collide with each other and you gain a lot of energy that is not as probable.

In short, what I am saying is, you think of a ball and it is somewhat of an inelastic ball and I throw it very, very hard at a wall, the probability is high that it is going to lose its energy. You will hear a loud thump and the ball is not going to do much. But the other way around where you have a ball that is just let us say floating around on a wall and it gains a lot of thermal energy because of collisions that is not as likely. So that is why we assume the, this frequency of, the collision factor is 1. So these two assumptions are applied here.

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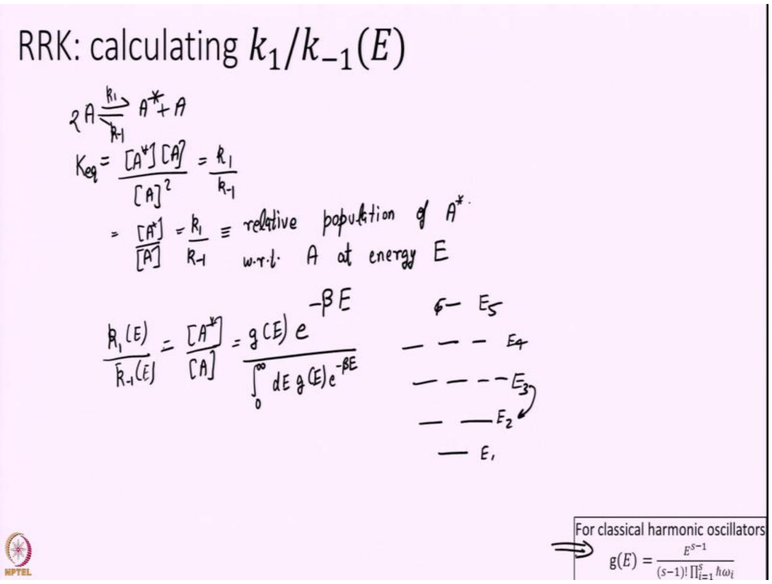

RRK: calculating $k_1/k_{-1}(E)$

$$2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$K_{eq} = \frac{[A^*][A]}{[A]^2} = \frac{k_1}{k_{-1}}$$

$$= \frac{[A^*]}{[A]} = \frac{k_1}{k_{-1}} \equiv$$ relative population of A^* w.r.t. A at energy E

$$\frac{k_1(E)}{k_{-1}(E)} = \frac{[A^*]}{[A]} = \frac{g(E)\, e^{-\beta E}}{\int_0^\infty dE\, g(E) e^{-\beta E}}$$

For classical harmonic oscillators

$$\Rightarrow g(E) = \frac{E^{s-1}}{(s-1)!\prod_{i=1}^{s} \hbar\omega_i}$$

The final number is k1, but instead of finding k1, I will find k1 over K minus 1. K minus 1 I have already found. If I find k1 over k minus 1, I have also found k1. Why am I insisting on k1 over k1 minus now? The reason is think of this A in equilibrium with A star, so 2A plus A. So k equilibrium will be nothing but A star into A divided by A square is equal to A star over A, but k equilibrium is also equal to k1 over k minus 1. So k1 over k minus 1 has a neat interpretation. This is relative population of A star with respect to A. Concentration is nothing but moles by Volume. Volume is a constant. So I do not worry about volume.

So, what I am saying is how many, if I start with A, how many A star are there at that energy E? So I am looking at this energy E and I am finding how many A star are there. So how do I calculate this? Now, we have done a little bit of our stat mech and rate theories. Well, this relative population is nothing but e to the power of minus beta E. Right? Not right. There is a little factor that I am missing here. What is the factor? This we have discussed once before. This will be the challenge to you. What mistake have I made? Of course, partition function, but other than partition function, what other mistake, degeneracy, the density of states.

So, at that given energy g tells me the density that is already there at that energy or the degeneracy multiplied by the Boltzmann factor. So Boltzmann factor gives me the overall ratio of energies which energy is more prominent at a different energy. And g of E tells me within that energy how many states are there. So this divided by an integral of all energies that is my partition function now. So never forget degeneracy.

So, the idea is, let us say, you have one state here at, as I moving in energy and I have more states here. The point is, let us say, E4 has only very few states and E5 has only, even lesser state. So even though E3 is higher in energy than E2, it still might be more probable because there are just more states there.

So, you are just more likely to be found there. So it is a competition between how high the energy is and how many states are accessible at that energy. So you must multiply those together. Now for our given model, which is a bunch of harmonic oscillators, we already showed what this g of E is.

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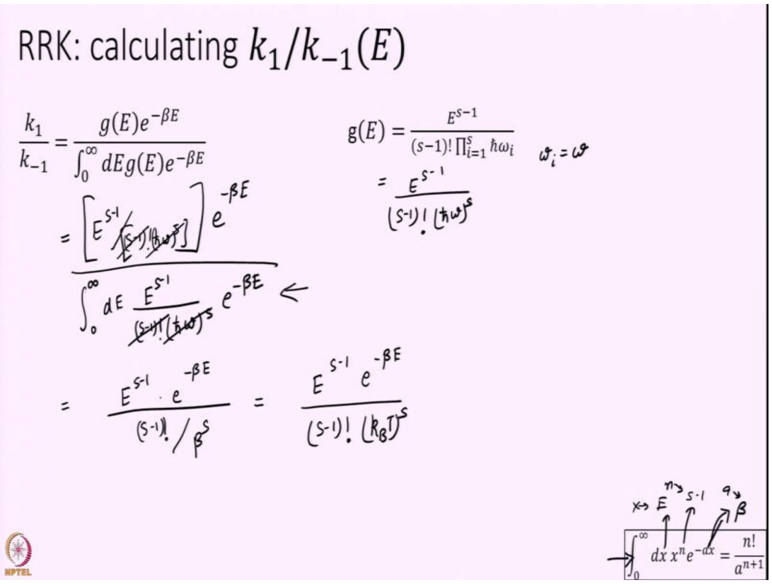

RRK: calculating $k_1/k_{-1}(E)$

$$\frac{k_1}{k_{-1}} = \frac{g(E)e^{-\beta E}}{\int_0^\infty dE\, g(E)e^{-\beta E}}$$

$$= \frac{\left[\frac{E^{s-1}}{\cancel{(s-1)!(\hbar\omega)^s}}\right] e^{-\beta E}}{\int_0^\infty dE\, \frac{E^{s-1}}{\cancel{(s-1)!(\hbar\omega)^s}}\, e^{-\beta E}} \leftarrow$$

$$= \frac{E^{s-1}\cdot e^{-\beta E}}{(s-1)!/\beta^s} = \frac{E^{s-1}\, e^{-\beta E}}{(s-1)!\,(k_B T)^s}$$

$$g(E) = \frac{E^{s-1}}{(s-1)!\prod_{i=1}^{s}\hbar\omega_i} \qquad \omega_i = \omega$$

$$= \frac{E^{s-1}}{(s-1)!\,(\hbar\omega)^s}$$

$x \to E$, $n \to s-1$, $a \to \beta$

$$\rightarrow \boxed{\int_0^\infty dx\, x^n e^{-ax} = \frac{n!}{a^{n+1}}}$$

So, what we are going to do is use this formula that we had used before and apply it to our expression here. Let me just make one simplification. This formula was calculated for a bunch of harmonic oscillators with different frequencies, but if all omega i’s are equal to some constant omega, then this becomes h bar omega to the power of s. That is our model that all oscillators have the same frequency.

So, this becomes e to the power of s minus 1 divided by s minus 1 factorial h bar omega to the power of s into e to the power of minus beta E divided by an integral 0 to infinity dE, e to the power of s minus 1 divided by s minus 1 factorial h bar omega to the power of s, e to the power of minus beta E. S minus 1 factorial and h bar omega are independent of energy. So I can cancel these out. This is equal to e to the power of s minus 1 into e to the power of minus beta E.

Now, look at what integral I am left with and I have given you a general rule to do this kind of integral. Here my x is nothing but E, n is nothing but s minus 1 and a is nothing but beta. So if I replace x with E, n with s minus 1 and a with beta, I will get exactly this integral here. So this integral then becomes n factorial, n is s minus 1 divided by a is beta to the power of s. Beta is nothing but 1 over kT. So this becomes this.

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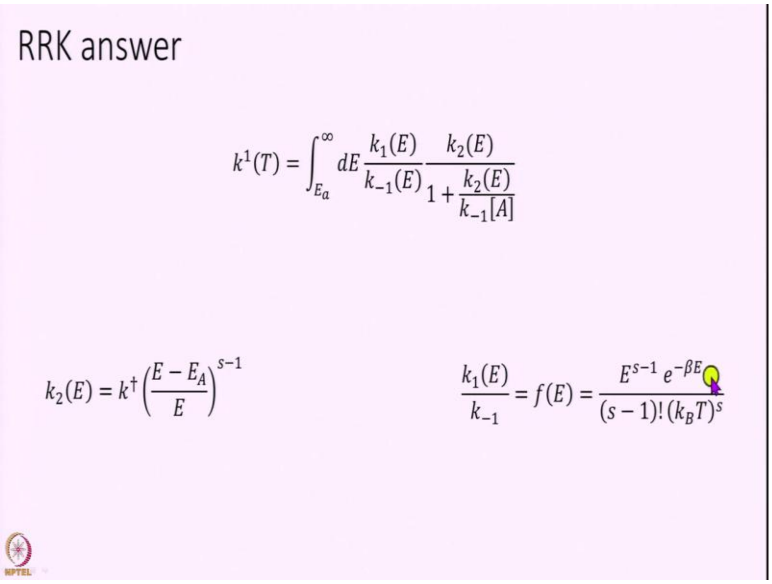

RRK answer

$$k^1(T) = \int_{E_a}^{\infty} dE \, \frac{k_1(E)}{k_{-1}(E)} \frac{k_2(E)}{1 + \frac{k_2(E)}{k_{-1}[A]}}$$

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

$$\frac{k_1(E)}{k_{-1}} = f(E) = \frac{E^{s-1} \, e^{-\beta E}}{(s-1)! \, (k_B T)^s}$$

So, now we have a full prescription to calculate the RRK answer. We want to integrate this integral in this integral. K2 we will use as this. We have not yet specified what this k dagger though is. So we will just do it. It is some constant, but how do I calculate that constant, I will tell you in a minute. K2 I calculate this way. K1 over k minus 1, I calculated in the last slide, and k minus 1, I calculate using collision theory. So I have all the components here. And I can just do this integration. If I cannot even do it analytically, then I can always use a computer to do this integration.

Another important thing to note, k1 over k minus 1 varies exponentially with energy. So that is my argument that when energy is much larger than barrier height the contribution will become very small, this exponential will become very, very small and dominant every other term. And this k1 over k minus 1 sits here. So that is why for energies that are much higher than barrier height, the contribution is always smaller. And that is why for those terms is k minus 1 even if it is changing with energy did not matter.

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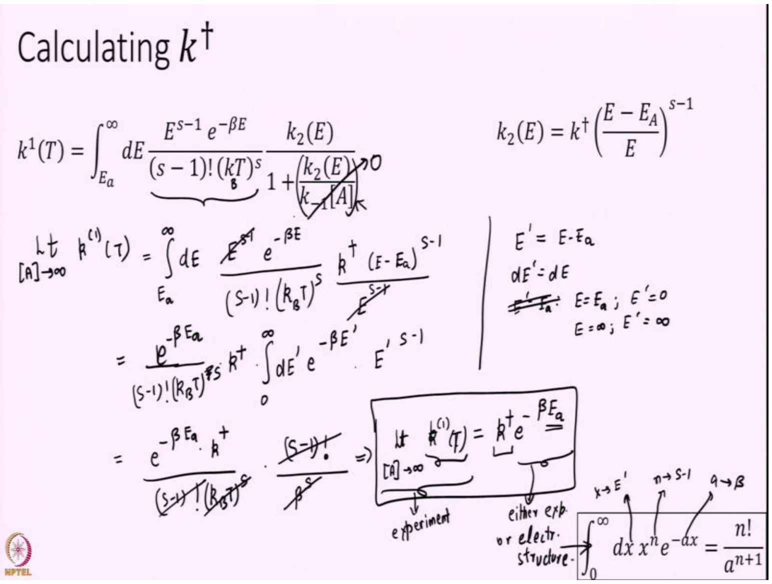

Calculating $k^{\dagger}$

$$k^{1}(T)=\int_{E_a}^{\infty} dE\, \underbrace{\frac{E^{s-1}\, e^{-\beta E}}{(s-1)!\,(k_BT)^{s}}}\, \frac{k_2(E)}{1+\cancel{\left(\frac{k_2(E)}{k_{-1}[A]}\right)}\to 0}$$

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

$$\lim_{[A]\to\infty} k^{(1)}(T)=\int_{E_a}^{\infty} dE\, \frac{\cancel{E^{s-1}}\, e^{-\beta E}}{(s-1)!\,(k_BT)^{s}}\, \frac{k^{\dagger}\,(E-E_a)^{s-1}}{\cancel{E^{s-1}}}$$

$$=\frac{e^{-\beta E_a}}{(s-1)!\,(k_BT)^{s}}\, k^{\dagger}\cdot\int_{0}^{\infty} dE'\, e^{-\beta E'}\cdot E'^{\,s-1}$$

$$=\frac{e^{-\beta E_a}\cdot k^{\dagger}}{\cancel{(s-1)!}\,\cancel{(k_BT)^{s}}}\cdot\frac{\cancel{(s-1)!}}{\cancel{\beta^{s}}} \Rightarrow \boxed{\underbrace{\lim_{[A]\to\infty} \underbrace{k^{(1)}(T)}}_{\text{experiment}} = \underbrace{k^{\dagger}}\, \underbrace{e^{-\beta E_a}}}$$

either exp or electr. structure

$$E'=E-E_a$$

$$dE'=dE$$

$$\cancel{E'=E_a}\quad E=E_a;\ E'=0$$

$$E=\infty;\ E'=\infty$$

$x\to E'$ $n\to s-1$ $a\to\beta$

$$\int_{0}^{\infty} dx\, x^{n} e^{-ax}=\frac{n!}{a^{n+1}}$$

So, now let us look at this calculation of this k dagger that I have been avoiding so far. We have some expression here now. I have substituted k1 over k minus 1 right here. To calculate k dagger, I will do the following. I will take the limit concentration of A goes to infinite. A appears only here.

When A goes to infinite, A is in denominator here, this whole term becomes 0. So I am simply left with 1 in the denominator. So this is A to the, to infinite dE, E to the power of s minus 1, e to the power of minus beta E divided by s minus 1 factorial kT, let me make it clear kBT, better put Boltzmann name there, k2 is k dagger e minus Ea to the power of s minus 1. So, at least one term cancels here.

So, I am left with 1 over s minus 1 factorial kT to the power of s into k dagger into this integral. To do this integral, I am going to do substitution of variable. I am going to define E prime as E minus Ea, dE prime will be equal to dE. When E prime is equal to Ea, my bad, when E is equal to Ea, E prime will be 0.

When E is equal to infinite E prime will be infinite. So with that, I put 0 to infinite here, dE is dE prime. I write this as e to the power of minus beta E prime into e to the power of minus beta Ea. E to the power of minus beta Ea is a constant. So I have pulled it out of the integral. Into E minus Ea is E prime to the power of s minus 1.

So, I have gotten this into a form which I know how to integrate. It is the same integral I showed you a couple of slides ago. x is E prime, n is s minus 1 and a is beta. So I get this as e to the power of minus beta Ea into k dagger divided by s minus 1 factorial kT to the power of s into this integral is n factorial, n is nothing but s minus 1, s minus 1 factorial divided by a to the power of n plus 1, a is nothing but beta to the power of s. So this terms cancel, no surprise. This also cancels.

So, this is implies limit A going to infinite of k1 is equal to. So this is an experimental recipe to calculate k dagger. We find this k1 experimentally at high concentration of A or high pressure of A. A is usually a gas. So, either way, even if you are in a solution, you can just make the concentration of A high.

If you are in a gas, you make the pressure of A high. And then you calculate this k1 and then you can calculate Ea with aid of some electronic structure calculation and then from that you calculate k dagger. So this portion comes from typically experiment and this portion will typically come from either experiment or electronic structure calculation. And once you have these two quantities, you can then calculate k dagger.

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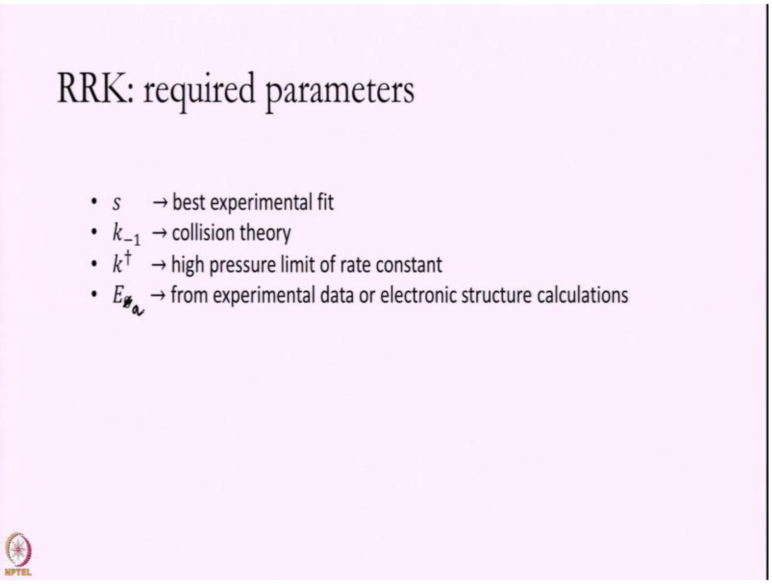

RRK: required parameters

- s → best experimental fit
- k_{-1} → collision theory
- $k^{\dagger}$ → high pressure limit of rate constant
- E_a → from experimental data or electronic structure calculations

So, in short, what are the parameters that are required to do an RRK calculation for unimoleculer decay? First is s, the number of oscillators that, unfortunately, is ad hoc. We calculate the RRK rate for different values of s and for whichever s the fit matches best with the experiment that is the value of s that we take. K minus 1 comes from collision theory. K dagger comes from high pressure limit of rate constant calculated experimentally.

So that is another unfortunate feature that you have to rely on experiment and you cannot calculate everything from calculations. And E naught or Ea I have been using, so I should stick to my notation. It is the, it comes from either experimental data or electronic structure calculations. That is the barrier height of course.

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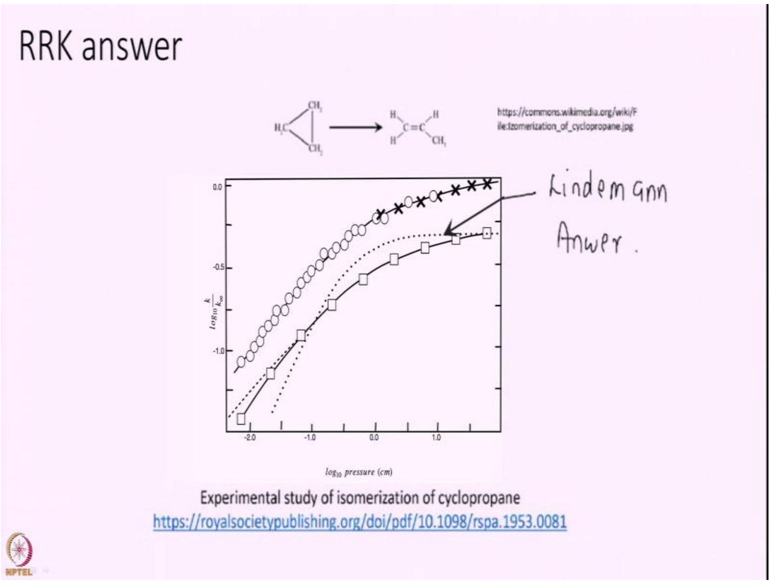

RRK answer

https://commons.wikimedia.org/wiki/File:Izomerization_of_cyclopropane.jpg

Experimental study of isomerization of cyclopropane

https://royalsocietypublishing.org/doi/pdf/10.1098/rspa.1953.0081

So, let me just show you one comparison against experiment. This is a very famous paper. The original paper was in 1920s or 30s. I cannot remember. So this is the isomerization of cyclopropane. That was the big puzzle of that day in 1910s and 20s. That is the problem that everybody was trying to crack. The experimental data is given by this solid line with these squares.

If you use the Lindemann answer, which is the one which is you, what you calculate with k1, k2 and k minus 1 at constant temperature, what we were doing earlier, then you see some deviation. Not a huge deviation agreeably, but not exactly right as well. Now when we apply RRK theory for s equal to 13, no good reason why s should be 13 by the way. It just happens that s is equal to 13, you get that result which is almost matches the experimental answer over a very wide range of pressure. So in the x-axis we have essentially log of pressure which is nothing but proportional to log of concentration. So you can find more details in this paper as well, very famous paper.

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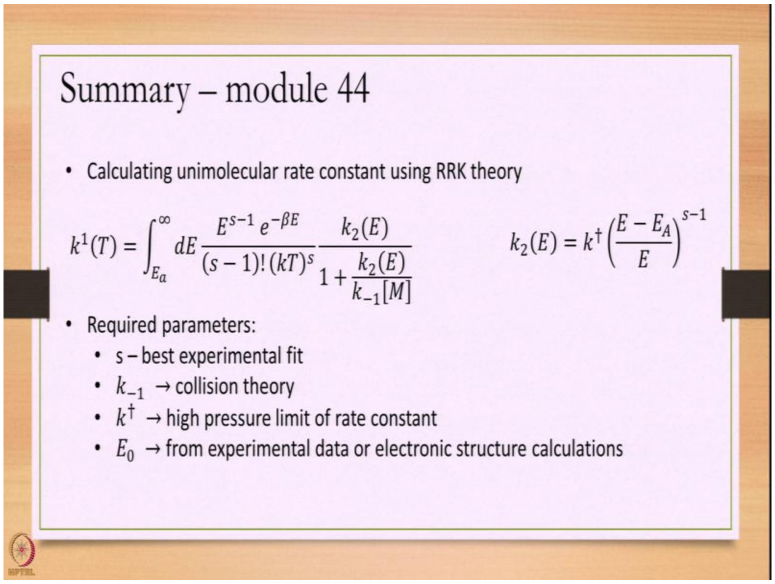

Summary – module 44

- Calculating unimolecular rate constant using RRK theory

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

- Required parameters:
  - s – best experimental fit
  - k_{-1} → collision theory
  - $k^{\dagger}$ → high pressure limit of rate constant
  - E_0 → from experimental data or electronic structure calculations

So, with that, I summarize today that we have shown how to calculate the unimolecular decay rate constant using RRK model. Our model comprises a bunch of harmonic oscillators with a same frequency. And within that model, we have a few parameters. We need to find s, which comes rather adhocly, k minus 1 comes from collision theory, k dagger typically comes from high pressure limit of rate constant and E naught or Ea, which is the barrier height, come from either experimental data or electronic structure calculations. With these, you can calculate k2, k minus 1 and k1 and calculate this integral using a computer usually and calculate k1. Thank you very much.