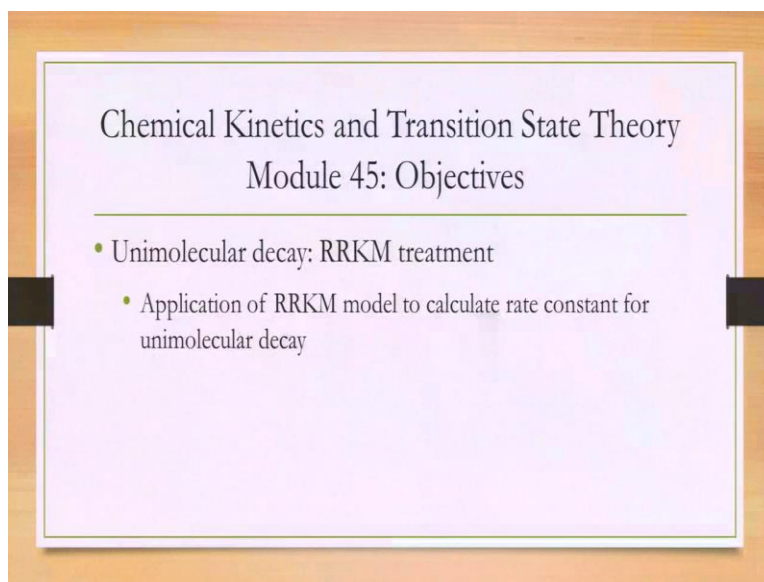


Chemical Kinetics and Transition State Theory
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Lecture 45
Unimolecular decay: RRKM's approach

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Hello, and welcome to module 45 of Chemical Kinetics and Transition State Theory. In the last module, we discussed the RRK way of looking at unimolecular decay. We had in two modules ago shown that very naive way of doing unimolecular decay does not match with experiment exactly. (0:46) had presented a different model on how to calculate unimolecular rate constant.

Today, we are going to do even better. What we had learnt in the last module is that it can do very well, but there are a few parameters that come ad hoc. That we fit so that you get the best match with experiment. But that is not very satisfactory. We should be able to get everything looking at the molecule. I should not rely on experimental data at all. I should be able to calculate everything.

So, today, we will look at what Marcus had to say about it. So, Marcus, again, was a brilliant theoretician. He was essentially given this problem that was discussed that earlier people RRK had solved in 1920s, late 1920s and it was left like that. Marcus in 50s was given this problem

essentially as a starting problem of his postdoc and he was asked let us see what you make of it. And this is what Marcus made of it. He basically cracked it in one or two years. Completely give the final correct answer. So, we will look at what Marcus had to say.

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Unimolecular rate constant

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

$A \xrightarrow{k^1} B$
 $\text{rate} = k^1[A]$

$2A \xrightleftharpoons[k_{-1}]{k_1} A^* + A$
 $A^* \xrightarrow{k_2} B$

Energy diagram showing states A, A*, and B. Energy levels are indicated by horizontal lines. The transition state barrier from A to A* is labeled R_1 , and the barrier from A* to B is labeled R_2 . The energy difference between A and B is labeled E .

Once more, let me revised for you what our problem is. So, our problem is we are studying A going to B with the overall rate constant k_1 . So, rate we have defined to be k_1 into concentration of A. Our mechanism is 2A going to A star plus A. A star going to B. Within this, we have discussed in a couple of modules that we can work out a rate constant, for this k_1 as this integral. The important point that I want to highlight is that A, A star which is an excited state and B, once more A star is not the transition state.

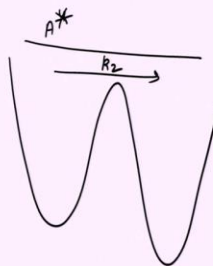
So, this is k_1 , this is k_{-1} and this is k_2 . So, the idea here in doing this integration is that we are calculating this k_1 , k_{-1} and k_2 at a given energy E . So, this is my energy E . So, I see, if I was that energy E , if k_1 excited me to that energy E , then my A star has a choice at that energy E to either move forward and become a product or come down and become A again.

So, this k_1 , k_{-1} and k_2 cannot be divorced away from each other. They must be calculated at that given energy E and not individually averaged out. So, with that, we had written this formula and in the last module, we looked at a way to calculating these numbers k_1 , k_2 and k_{-1} using the RRK model. So, let us look at what Marcus said.

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RRKM: calculating $k_2(E)$

$$k_{RRKM}(E) = \frac{W^\ddagger(E - E_a)}{hg_R(E)} = k_2(E)$$



The first thing is calculating k_2 that is one big thing that is different. Once more, I really like drawing these pictures. So, let me draw it again. k_2 is this one. So, this k_2 I am calculating at a constant energy. And I have already shown you that our RRK model is actually not very good at calculating this constant energy rate constants.

RRKM has to be used, which is much more elaborate, which makes much fewer assumptions which looks at the molecule much closer and includes all possible vibrations and rotations in a more intrinsic fashion. And with that we calculated a k RRKM by this formula where g is the density of states and W is the total number of states. So, this is what we are going to use for k_2 of E .

Unfortunately, there is no easy way to write this formula. You have to calculate W and g for each molecule. And that is the way it has to be. Each molecule is different. Each molecule has a different bunch of oscillators there. So, it is not a good idea to generalize all molecules as simply a bunch of harmonic oscillators at some frequency W . A more general formula has to be written that must be calculated differently for each molecule. So, that is point number one that is, which is different from RRK model.

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

Same as RRK

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

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

Assumptions in this calculation:

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



The second is k_{-1} , where Marcus made no change. It is exactly the same as RRK. We calculate this k_{-1} as the collision theory decay rate constant of losing energy from this highly excited energy E to coming down to the ground state at thermal energy. So, we discussed this in the last module. So, I am not going to elaborate too much in it. The rate constant given by collision theory is here.


And there are two critical assumptions. k_{-1} is not a function of energy. It is a function only of temperature. The picture again is that this energy will be close to activation energy, which is anyway a large amount of energy. So, small deviations around the activation energy does not matter. And if the deviation is too large, the rate constant will anyway be too small. So, again, it does not matter. So, for all practical purposes, I can calculate this k_{-1} as a constant.

The second thing is, there is no collision factor here. There is no, all collisions are supposed to be equally reactive. And that again, the underlying idea is that you are having a very large energy E anyway. And so if you are colliding, the probability of losing energy is always very high. So, all collisions are reactive in that sense.

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

$$\frac{k_1}{k_{-1}} = \frac{\overbrace{g(E)e^{-\beta E}}^{\text{Density} \cdot \text{Boltzmann}}}{\underbrace{\int_0^\infty dE g(E)e^{-\beta E}}_{\text{Partition Junction}}} \leftarrow 2A \xrightleftharpoons[k_{-1}]{k_1} A^* + A$$

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


The final picture is k_1 over k_{-1} . In RRK, we had written a very concrete expression for it. No such expression can be written here. We derived this expression in the last module. This comes from the picture that A and A^* , if this is k_1 , this is k_{-1} , so the k equilibrium is A^* by A , this is $2A + A$, which is equal to k_1 over k_{-1} . And this equilibrium constant is nothing but the relative population of A^* with respect to A .

So, that then can be calculated as the density at energy E into e to the power of minus beta E . That is the Boltzmann factor and that is the density. So, this is Boltzmann factor and this is density. So, again, to reemphasize, our population is a product of two numbers, of two quantities. One, which is Boltzmann factor, that is the overall weight of being at that energy E multiplied by how many states are accessible at that energy. So, it must be a product of those two.

In fact, even if the energy is high, but you just have a lot of states that are accessible at that energy, it still makes it more probable. And the denominator is, of course, the partition function net normalizes this probability. A partition function into some factor of H . Some normalization constant in short. Again, Marcus said, do not try to simplify this. There is no meaning in this. This g must be calculated for a molecule separately. You cannot generalize it. You cannot say that we have a general formula for all possible molecules. That attempt is not going to work.

So, for a given reaction, you better calculate g of E separately. And we have spent one module on looking at how to calculate this g . So, I am not going to repeat all of that. But again, we

divide g into rotations and vibrations and we figure out ways on how to calculate rotational g and vibrational g for vibration. We often do sum of states. Rotations can be treated classically. All of this was discussed earlier. So, you can go back and have a look at that module again on how to calculate g .



But all Marcus is saying is it is upon you. How you can calculate this g ? How accurate g you want. But I am not going to give you a common prescription for all molecules. That is just a bad way of looking at things. All molecules have their own individual personalities. You do not go ahead and see to bunch all these molecules together.

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RRKM answer

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

$$k_2(E) = \frac{W^{\ddagger}(E - E_a)}{h g_R(E)}$$

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





So, that is pretty much RRKM answer. He all, Marcus is saying is let us keep things general. You keep, calculate this k_1 over k_{-1} , I should write R to the present reactant, A remember is a reactant. You calculate this k_1 over k_{-1} separately for each molecule. You calculate this k_2 separately for each molecule. k_{-1} he did not hinder. He said he will calculate using collision theory and do this integration. So, it is more manual. It is not an easy answer now.

RRK had given a much more simpler answer. That simpler answer often has problems. You have, this RRK answer was adhoc. We had to figure out what this s is. We have to figure out k_{\ddagger} experimentally. Here we are saying, we will look at each molecule and we will look at it very closely and we will get the answer right now and we will get it only by theory. We will not retort to experimental data.

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RRKM: required parameters


- k_{-1} → collision theory
- E_a → from experimental data or electronic structure calculations
- $W(E)$ and $g(E)$ → Structural information: frequencies and moment of inertia of reactants and TS (typically from electronic structure)




So, what are the required parameters now for RRKM? k_{-1} of course is coming from collision theory. Activation energy can come from experimental data or you can do an electronic structure calculation these days. Back in Marcus' day that was much harder, but now things are very different. You can actually ask the computer to get what this activation energy is. W and g comes from the very refined structural information of that particular molecule which usually comprises of frequencies, the vibrational frequencies and moment of inertias. Moment of inertia of course, for calculating rotational g and W and frequency is for vibrational g and W . Here we do not resort to experiment.

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RRK vs. RRKM



- RRKM is a more general theory
- RRK considers a specific model of s harmonic oscillators, all with same frequency and does not include rotations
- RRKM considers the actual vibrational and rotational modes of the molecule
- RRK requires adhoc fitting of experimental data. RRKM does not




So, RRKM is a more general theory compared to RRK. RRK is actually a special limit of RRKM and I will show that in the next slide. RRK is a very specific model of s harmonic oscillators all with the same frequency and s is arbitrary in RRK. We choose the s that matches the experiment the best rather than the other way around. RRKM looks at, properly at the vibrational and rotational modes. RRK requires adhoc fitting of experimental data, RRKM does not.

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Calculating the RRKM rate constant for the RRK model

$$k^{\ddagger}(T) = \int_{E_a}^{\infty} dE \frac{k_1(E)}{k_{-1}(E)} \frac{k_2(E)}{1 + \frac{k_2(E)}{k_{-1}[A]}}$$
$$k_2(E) = \frac{W^{\ddagger}(E - E_a)}{h g_R(E)}$$
$$\frac{k_1}{k_{-1}} = \frac{g_R(E) e^{-\beta E}}{\int_0^{\infty} dE g(E) e^{-\beta E}}$$

RRK: no rotations
 s harmonic oscillators with freq. ω .



So, let me just point out one special thing that I said in the last slide, which is that RRK is a special case of RRKM. So, let us look at RRKM theory and apply it to the RRK model. RRK

model is no rotations, s harmonic oscillators with frequency omega, all with the same frequency. So, we have a general prescription now given by this k2 and k1 over k minus 1. So, let us calculate this general prescription for this specific model.

K1 one over k minus 1, I really do not need to, because we have already calculated k1 over k minus 1 using this specific formula only when we were deriving RRK formula. So, you will end up getting the same formula that we had derived two modules ago, last module actually, I am sorry. K1 over k minus 1 was already derived with this formula and for this particular model. So, let us not discuss that. Let us look at k2.

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Calculating the RRKM rate constant for the RRK model

$$k_2(E) = \frac{W^\ddagger(E - E_a)}{h g_R(E)}$$

$W^\ddagger \rightarrow$ total num. of states excluding rxn. coord.

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

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

$$k_2(E) = \frac{1}{h} \left(\frac{E - E_a}{E} \right)^{s-1} \cdot \frac{(\hbar\omega)^s}{(\hbar\omega)^{s-1}}$$

$$= \frac{\hbar\omega}{h} \left(\frac{E - E_a}{E} \right)^{s-1}$$

$$= \frac{\omega}{2\pi} \left(\frac{E - E_a}{E} \right)^{s-1}$$

$W(E) = \frac{E^s}{s! \prod_{i=1}^s \hbar\omega_i} = \frac{E^s}{s! (\hbar\omega)^s}$ (All $\omega_i = \omega$)

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

$k_2^{RRK}(E) = k^\ddagger \left(\frac{E - E_a}{E} \right)^{s-1}$

$k^\ddagger = \frac{\omega}{2\pi}$

rxn coord

k2 actually looks very different now. It looks like some W dagger over hgR where k2 RRK we showed was equal to this. Are they the same thing written in different languages? Let us find out. W dagger, they, here we have to be extremely careful. This is a very common mistake that almost everybody makes. W dagger is total number of states excluding reaction coordinate. So, this total number is calculated for one degrees of freedom less than the total degrees of freedom.

So, let me just write W of E as E to the power of s divided by s factorial into h bar omega to the power of s, because all omega i's equal to omega in my specific model of RRK. Arbitrarily I call the first mode as a reaction coordinate. You are free to choose the 13th mode as reaction coordinative if 13 is your favorite number. So, this is equal to E to the power of s minus 1, one

degree of freedom less compared to total. Not even this, I have made a mistake, so let me correct my mistake. It is $E - E_a$.

So, I am calculating W dagger at $E - E_a$. So, $E - E_a$ to over $s - 1$ divided by s factorial h bar, I am making the same mistake, I told you everybody makes this mistake. So, do I. I am not immune to it either. $S - 1$ factorial h bar ω to the power of $s - 1$. So, instead of using s , we must use $s - 1$.

g_R is the same. g_R will have all s h bar ω with the power of s . Again, this factor will become h bar ω to the power of s . So, I have W and I have g , I have to just divide these two. You get $E - E_a$ divided by E to the power of $s - 1$. You already start noticing that we are getting terms similar to this. $S - 1$ factorial will cancel when I divide these two. h bar ω will not cancel. I will get h bar ω to the power of s divided by h bar ω to the power of $s - 1$. So, I am left with 1 h bar ω . So, I am left with h bar ω divided by h into $E - E_a$. h bar is nothing but h over 2π .

So, this is a very neat result we get. Compare these two results. So, when I compare these two results, I get k dagger is equal to ω over 2π . So, RRKM is even giving a prescription to RRK. He is saying you do not have to remember. Earlier for RRK we had said that to calculate k dagger we have to look at experimental data at large pressure or concentration. RRKM comes in and since you do not know what I can tell you even a better answer. The frequency, that common frequency that you had chosen, k dagger is nothing but ω over 2π .

So, it is a very neat picture and it makes sense as well, because ω over 2π , well, is also the frequency of my reaction coordinate. All coordinates have same frequency. So, this is let us say my reaction coordinate. And k dagger should represent this frequency somehow. ω over 2π is the number of times I hit the barrier height at per unit second. So, this must appear somehow and RRKM shows that it does appear properly. So, I do this general prescription and ω over 2π comes very naturally.


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Lindemann vs. RRK vs. RRKM

$$A+M \xrightleftharpoons[k_{-1}]{k_1} A^*+M$$

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

	Lindemann	RRK	RRKM
Rate constant $k(T)$	$\frac{k_2(T)k_1(T)/k_{-1}(T)}{1 + \frac{k_2(T)}{k_{-1}(T)[M]}}$	$\int_{E_a}^{\infty} dE \frac{k_2(E)k_1(E)/k_{-1}}{1 + \frac{k_2(E)}{k_{-1}(T)[M]}}$	
	k_1 and k_2 are independent	k_1 and k_2 are concerted	
Model		s harmonic oscillators with no rotations	Full vibrational structure including rotations
Required Input	k_1, k_{-1}, k_2	s, k_{-1} , E_a , k^\ddagger s - educated guess, best fit k_{-1} - From collision theory (pre-exponential factor) E_a - from experiment/electr. structure k^\ddagger - high pressure limit; frequency of reaction coord.	k_{-1} , E_0 + Structural information: frequencies and moment of inertia of reactants and TS (typically from electronic structure)



So, I have given you a big comparison of the three different ways of calculating this unimolecular decay rate constant. The Lindemann version is what was the original model. I look at k_1 , k_2 and k_{-1} as a function of temperature. I do not look at them in a correlated fashion. As, do my simple kinetics, use steady state hypothesis and get my answer. The required input for this, of course, is k_1 , k_{-1} and k_2 that you can calculate in different ways. But we know that this does not match well with experiment. We have to do better than this.

So, RRK in '27 and '28 gave a different prescription that you must integrate over all possible energies instead of looking at k_1 and k_2 independently. They are correlated. You calculate them at a given energy and integrate over all possible energies. So, k_1 and k_2 are concerted and that is also true in RRKM. They both start with the same formula. RRK specifically assumes that my molecule consists of s harmonic oscillators with no rotations and all harmonic oscillators have the same frequency.

So, the required parameters for RRK is this s, which is usually given by the best fit, k_{-1} that comes from collision theory, E_a is simply the barrier height that can come either from experiment or electronic structure and k^\ddagger can either come from high pressure limit or as we understand it, we, it can be looked at as $\omega / 2\pi$, which is the frequency of the reaction coordinate.

RRKM that is slightly better. S should not be needed. S is nothing but the total number of vibrational modes. I will remove s, that is my bad. It requires k minus 1 which comes from collision theory. And E naught of course also is needed which comes from experimental data or electronic structure calculations. But beyond that, we calculate g and W for RRKM which requires structural information of reactant and transition state such as frequencies and moment of inertia, which will typically come from electronic structure calculations. They can also come from experiment if you want.

So, RRKM is a more advanced model and is very actively used till today. One point let me just add since we are at the end of it. There is a difference between R, R and K by the way, R and R were Rice and Ramsperger and K was Kassel. R and R calculate this k2 classically. They follow all the same prescription like this, all three of them are R, R and K, but Kassel was actually the first person to highlight that k2 should be calculated using quantum mechanics and you will get a better answer. But nonetheless even k, even if he got the better answer, he has to calculate this s rather adhocly. It does not matches correctly.

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Summary – module 45

- Calculating unimolecular rate constant using RRKM theory

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

$$k_2(E) = \frac{W^\ddagger(E - E_a)}{hg_R(E)}$$

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

- RRKM theory is a more general and improved model over RRK theory

So, today we have looked at a comparison of RRK and RRKM theory. We have looked at how we can, RRK and RRKM both improve over Lindemann and RRKM improve over RRK. And RRKM is giving the most general prescription. It requires more hard work. You have to look at each molecule separately. RRKM said that there is no easy prescription. Each molecule is, has its

own individual personality and he must calculate its rate constant accordingly. Thank you very much.