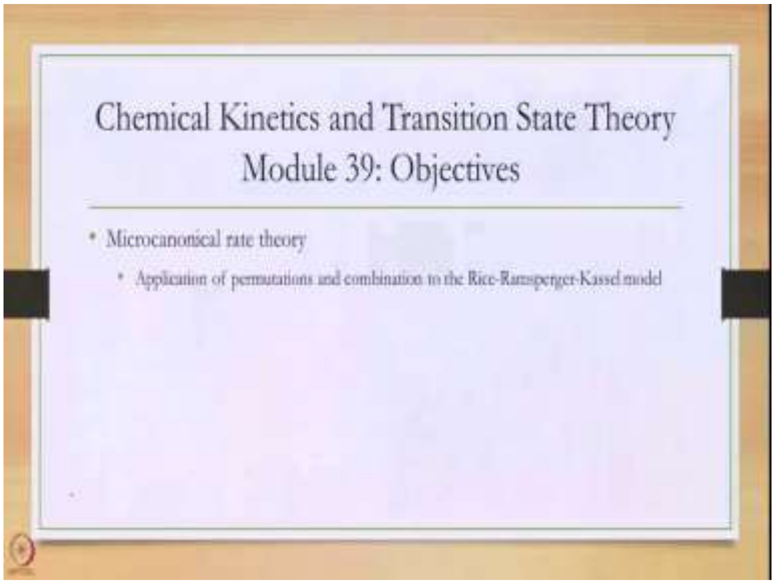
Chemical Kinetics and Transition State Theory
Professor Amber Jain
Department of Chemistry,
Indian Institute of Technology Bombay
Lecture 39
Microcanonical rate constant: RRK model

(Refer Slide Time: 00:16)

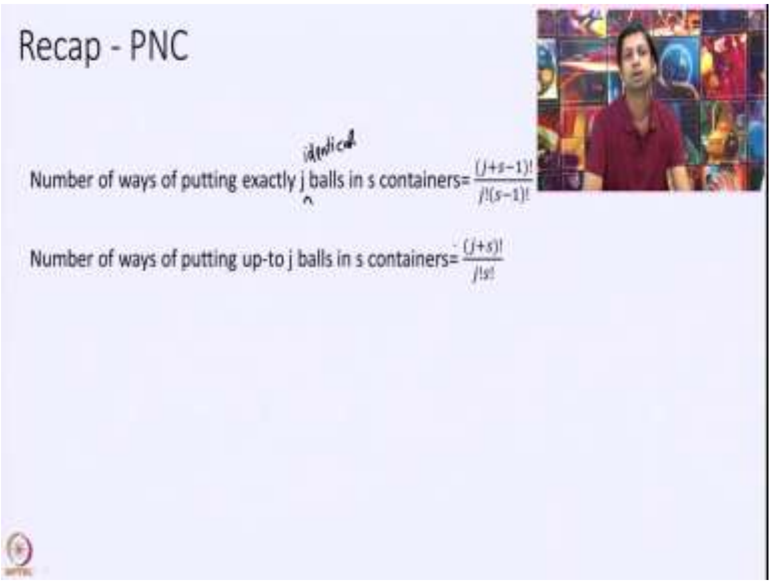


Chemical Kinetics and Transition State Theory
Module 39: Objectives

- Microcanonical rate theory
  - Application of permutations and combination to the Rice-Ramsperger-Kassel model

Hello, and welcome to module 39 of Chemical Kinetics and Transition State Theory. This is really a continuation of the last module. In the last module, we discussed a simple model to calculate rate constant at a given energy and we took a little detour of permutations and combinations and today we will apply these permutations and combinations to calculate rate constant.

(Refer Slide Time: 00:46)



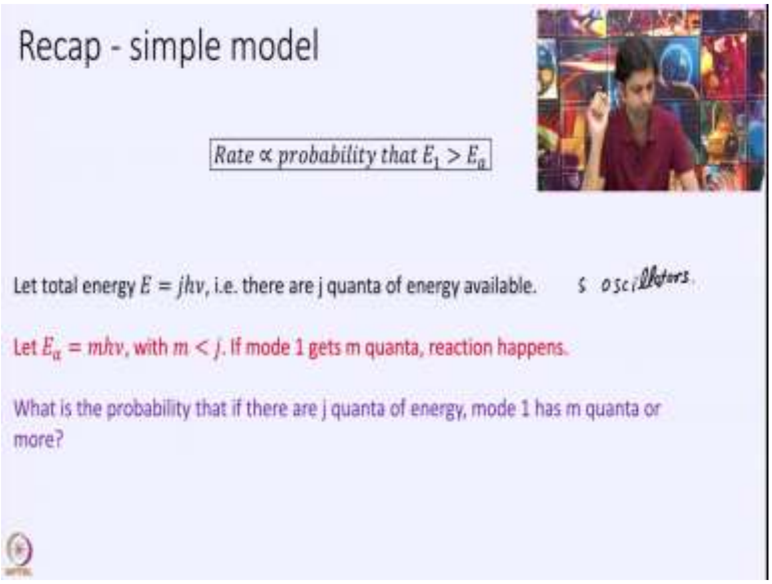
Recap - PNC

Number of ways of putting exactly $\overset{\text{identical}}{j}$ balls in s containers= $\frac{(j+s-1)!}{j!(s-1)!}$

Number of ways of putting up-to j balls in s containers= $\frac{(j+s)!}{j!s!}$

So a little recap of what we looked into the permutations and combinations. The number of ways of putting exactly j identical balls, so let me just write identical to be more precise, in s distinct containers is given by this expression, this factorials. And number of ways of putting up to j balls in s containers is given by this expression.

(Refer Slide Time: 01:16)



Recap - simple model

$\boxed{Rate \propto probability\ that\ E_1 > E_a}$

Let total energy $E = jh\nu$, i.e. there are j quanta of energy available. s oscillators.

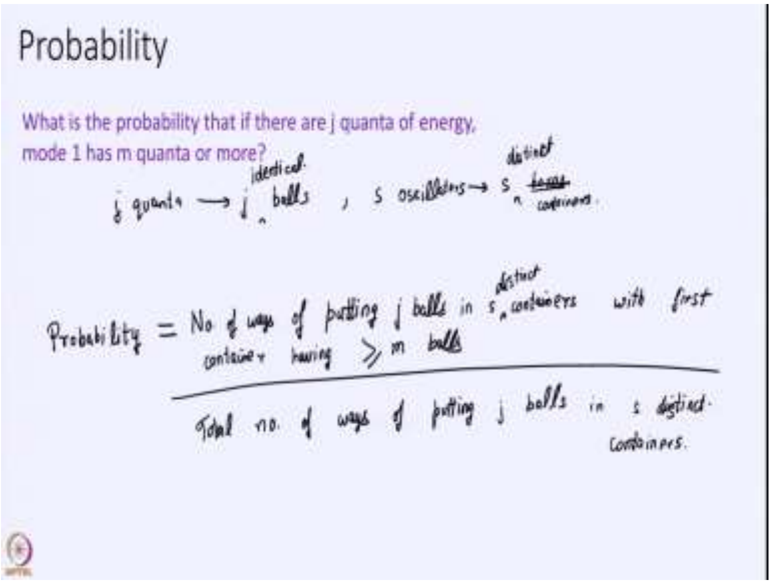
Let $E_a = mh\nu$, with $m < j$. If mode 1 gets m quanta, reaction happens.

What is the probability that if there are j quanta of energy, mode 1 has m quanta or more?

We had also discussed a simple model of calculating rate constant at a given energy. The rate we assume is proportional to the probability that E1 which is the energy mode 1 is greater than Ea, which is some activation energy, a parameter in the system for our problem.

So let us assume that the total energy E corresponds to some quanta jh nu and Ea is given by some m quanta of energy. So what we are really asking is, what is the probability that if I distribute j quanta among s oscillators, so one thing I have forgotten to mention here or recap, there are s oscillators. And so we are putting these j quanta in s oscillators and what is the probability that the first mode will get m quanta or more.

(Refer Slide Time: 02:21)



Probability

What is the probability that if there are j quanta of energy, mode 1 has m quanta or more?

j quanta → j identical balls , s oscillators → s distinct ~~boxes~~ containers.

$$\text{Probability} = \frac{\text{No of ways of putting j balls in s distinct containers with first container having} \geq \text{m balls}}{\text{Total no. of ways of putting j balls in s distinct containers.}}$$

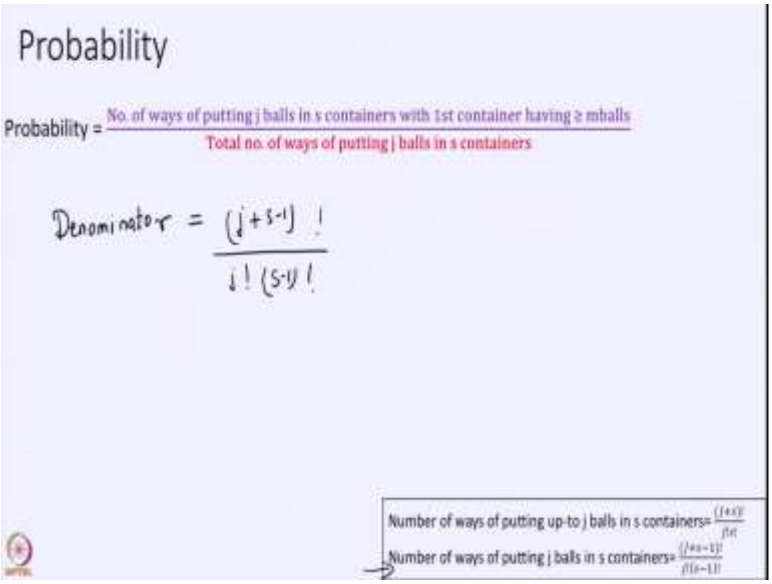
So today we are going to calculate this probability. So we have to get back to our PNC to calculate this probability. What we are doing is we are looking at j quanta as essentially j balls, j identical balls. All quanta are identical. We cannot distinguish between two different quanta of energy. S oscillators represent to me s boxes.

So the problem is of putting j identical balls in s distinct boxes, containers. Let me just use the word container because that is what I have used so far. And I am asking you what is the probability that first mode gets more than m balls? So how do I calculate this probability?

This probability is given by a number of ways of putting j balls, they are all identical, so I am not going to repeat identical all the time, of putting j identical balls in s distinct containers with first container, so these are distinct, first container having greater than or equal to m balls divided by total number of ways of putting j balls in s distinct containers.

So that is how you calculate probability. In the denominator you put all possibilities and in the numerator you put only favorable possibilities. So the numerator contains all possibilities which has m or more balls in the first container and the denominator has all possible ways of distributing. We find the ratio that is simply my probability.

(Refer Slide Time: 05:05)



Probability

$$\text{Probability} = \frac{\text{No. of ways of putting j balls in s containers with 1st container having} \geq \text{m balls}}{\text{Total no. of ways of putting j balls in s containers}}$$

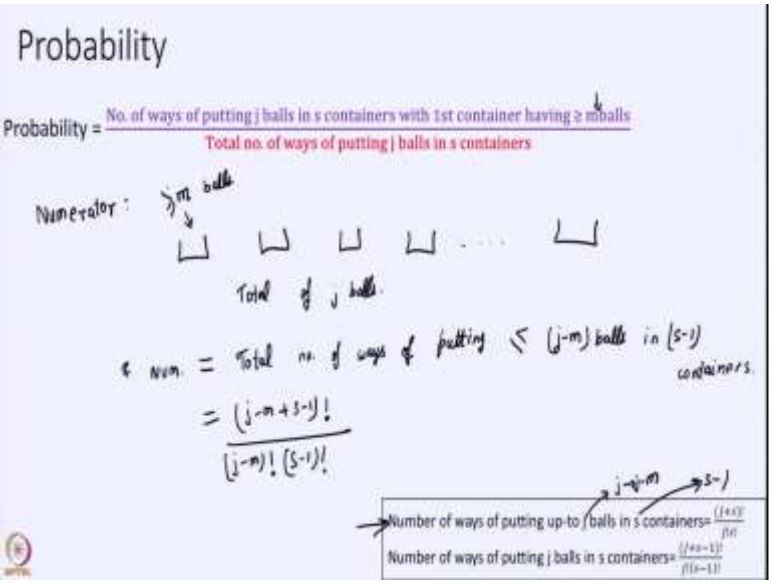
$$\text{Denominator} = \frac{(j+s-1)!}{j!\,(s-1)!}$$

Number of ways of putting up-to j balls in s containers= $\frac{(j+s)!}{j!s!}$

Number of ways of putting j balls in s containers= $\frac{(j+s-1)!}{j!(s-1)!}$

So let us calculate the denominator and the numerator. The denominator is rather trivial. So let us calculate that first. We like doing easy things first. So denominator is simply the total number of ways of putting j identical balls in s distinct containers. Here, we already calculated it last time. So this is simply equal to j plus s minus 1 factorial divided by j factorial s minus 1 factorial, good, done.

(Refer Slide Time: 05:39)



Probability

$$\text{Probability} = \frac{\text{No. of ways of putting j balls in s containers with 1st container having} \geq \text{m balls}}{\text{Total no. of ways of putting j balls in s containers}}$$

Numerator : $\geq m$ balls

Total of j balls.

$\therefore$ Num. = Total no. of ways of putting $\leq (j-m)$ balls in $(s-1)$ containers.

$$= \frac{(j-m+s-1)!}{(j-m)!\,(s-1)!}$$

Number of ways of putting up-to j balls in s containers= $\frac{(j+s)!}{j!s!}$

Number of ways of putting j balls in s containers= $\frac{(j+s-1)!}{j!(s-1)!}$

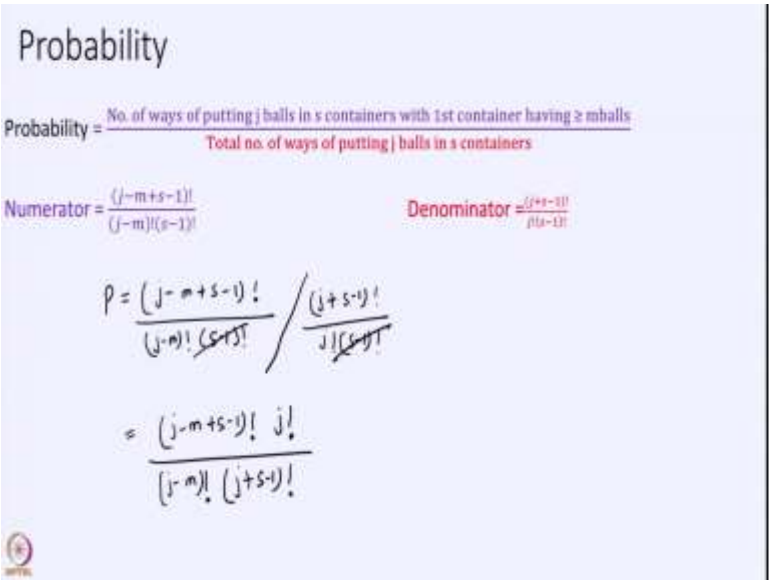
Numerator, this is slightly tricky. So we will be careful. Numerator is number of ways of putting j balls in s containers with the first container greater than having more than or equal to m balls. There is supposed to be a space here. So how do I do this? This is again a puzzle for you. You can take a little pause and try to calculate this on your own.

If you like solving these kind of permutations and combinations. I find them a lot of fun. So I have a s containers with me and I am asking the question, this one should have more than or equal to m balls and I have a total of j balls, how many ways can I arrange this so that the first one have at least m balls? Well, the answer is actually simple.

The total number of ways the numerator is nothing but total number of ways of putting less than or equal to j minus m balls in s minus 1 containers. So, the first one has m or more, which implies that the rest of them combined have j minus m or less. If the first box has m balls, the rest of them will have j minus m exactly. If the first one has m plus 1, the rest of them will have j minus m minus 1.

So the maximum you can put in this s minus 1 containers is j minus m, so it will be less than or equal to j minus m. You can have 0 as well. I can perhaps put all of the balls in the first container that has also a configuration. So this thing, well, is this one with j replaced with j minus m and s replaced with s minus 1. So I get j minus m plus s minus 1 factorial divided by j minus m factorial s minus 1 factorial.

(Refer Slide Time: 08:22)



Probability

$$\text{Probability} = \frac{\text{No. of ways of putting j balls in s containers with 1st container having} \geq \text{m balls}}{\text{Total no. of ways of putting j balls in s containers}}$$

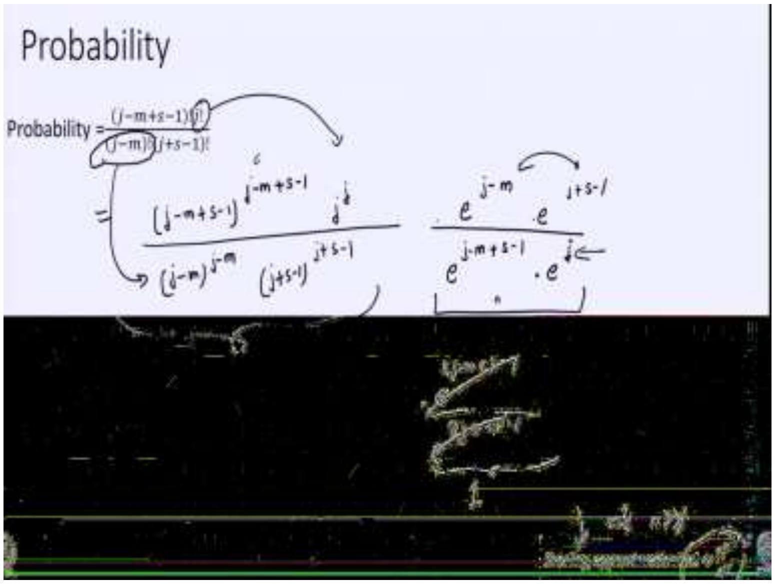
$$\text{Numerator} = \frac{(j-m+s-1)!}{(j-m)!(s-1)!} \qquad \text{Denominator} = \frac{(j+s-1)!}{j!(s-1)!}$$

$$P = \frac{(j-m+s-1)!}{(j-m)!\,\cancel{(s-1)!}} \Big/ \frac{(j+s-1)!}{j!\,\cancel{(s-1)!}}$$

$$= \frac{(j-m+s-1)!\; j!}{(j-m)!\; (j+s-1)!}$$

So now I have the numerator and I have the denominator. So, I will find the probability now as the division of the two. Factorial s minus 1 factorial divided by j plus s minus 1 factorial divided by j factorial s minus 1 factorial. You notice at least one term cancels. That is good news for us. So what I am left with is j factorial comes to the numerator.

(Refer Slide Time: 09:10)



Probability

$$\text{Probability} = \frac{(j-m+s-1)!\,j!}{(j-m)!\,(j+s-1)!}$$

$$= \frac{(j-m+s-1)^{j-m+s-1}\; j^{j}}{(j-m)^{j-m}\; (j+s-1)^{j+s-1}} \; \frac{e^{j-m} \cdot e^{j+s-1}}{e^{j-m+s-1} \cdot e^{j}}$$

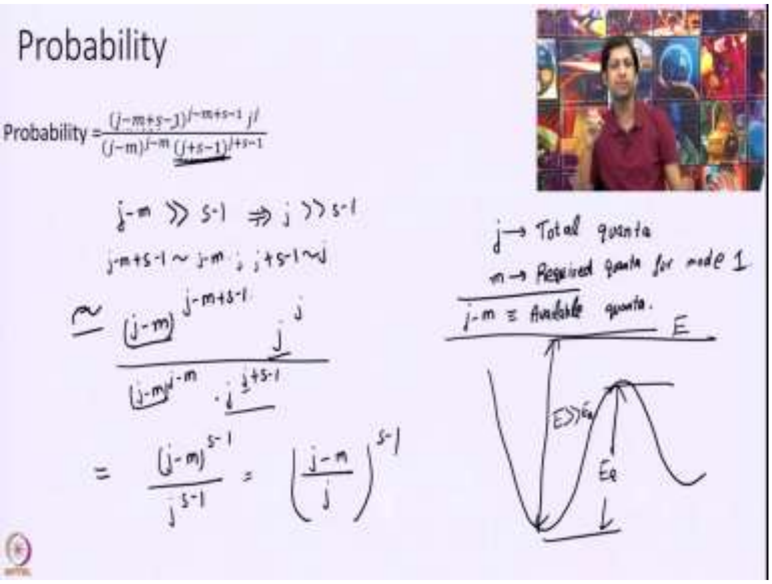
Now we are going to make an approximation. So far what we have done was an exact permutation and combination, but we lead to these factorials which do not simplify anymore. But we can simplify things a little bit if we use this thing called a Stirling approximation here. This is true only when n is large. So what we are going to assume essentially is that j is large.

We have a lot of energy. So what we are working today this RRK model holds only when there is a lot of energy. That is our first approximation. We are going to make one more. So we are going to use this n factorial equal to n to the power of n over e to the power of n. So let us write things very, very carefully, to the power of j minus m plus s minus 1. And I will have a corresponding exponential as well.

Exponentials I am going to write here, e to the power of j minus m plus s minus 1. So this is n to the power of n term. This is e to the power of n term. I have j factorial now. J factorial gives me j to the power of j divided by e to the power of j. J minus m factorial will give me j minus m to the power of j minus m into exponential of j minus m. J plus s minus 1 factorial now is j plus s minus 1 to the power of j plus s minus 1 into e to the power of j plus s minus 1.

Let us look at the exponential part for a moment. This is equal to e to the power of j minus m, 2j minus m plus s minus 1, I am adding these two together, divided by e to the power of 2j minus m plus s minus 1, I am adding these two together in the denominator. Well, that is equal to 1. So something good happened at least. And I am simply left with this term.

(Refer Slide Time: 11:26)



Probability

$$\text{Probability} = \frac{(j-m+s-1)^{j-m+s-1}\, j!}{(j-m)^{j-m}\, \underline{(j+s-1)}^{j+s-1}}$$

$$j-m \gg s-1 \Rightarrow j \gg s-1$$

$$j-m+s-1 \sim j-m \,;\, j+s-1 \sim j$$

$$\simeq \frac{(j-m)^{j-m+s-1}\, j^{j}}{(j-m)^{j-m} \cdot j^{j+s-1}}$$

$$= \frac{(j-m)^{s-1}}{j^{s-1}} = \left(\frac{j-m}{j}\right)^{s-1}$$

j → Total quanta

m → Required quanta for mode 1

j-m ≡ Available quanta.

What do I do now? It is still a very complex term. Our next assumption is slightly more intricate. We are going to assume j minus m is much, much greater than s minus 1. This assumption essentially tells what is j and m, let us remind ourselves, j represents total number of quanta, m represents required quanta for mode 1. So, this difference is available quanta basically. So m is the necessary quanta. So I am saying I have a lot more quanta than you absolutely require.

In short, if this is my reaction coordinate and this is Ea, I am saying that the total energy is much more than Ea. So E represents a total quanta available and Ea represents the quanta that is absolutely necessary. So I am saying E is much, much greater than Ea. In fact, it is much, much greater than this difference compared to the number of possibilities I can distribute against. So that is the approximation we make.

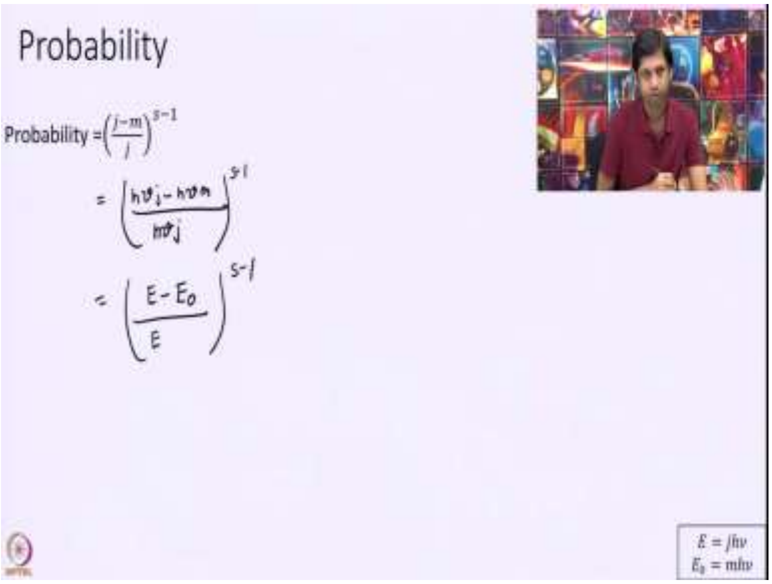
Under that approximation, if this is true, I can also assume j is much, much greater than s minus 1 as well. If this is true, this is of course true, m is remember positive. So what I am going to do, these are, slightly you have to be careful when you make these approximations only in the bases here. I will make the approximation. So I will assume j minus m plus s minus 1 is approximately j minus m. S minus 1 is negligible, but only in the base.

Remember, when you take powers, you still have a much larger effect of the errors. So we do not make this approximation in the power, but only in the base. What I am saying effectively is, instead of saying it is 10 to the power of, let us say 100 to the power of 100, it is 99 to the power of 100. But if I make it 99 to the power of 99, then I am introducing a much bigger error. The powers make a much bigger impact is what I am saying.

So I approximate this as j minus m to the power of j minus m plus s minus 1. I retain j to the power of j, I retain j minus m to the power of j minus m. And this term I replace j plus s minus 1 as j. So I get j to the power of j plus s minus 1. So let me put it here, because I need more space there. So this is then equal to j minus m to the power of s minus 1 divided by j to the power of s minus 1. You notice that this is j minus m, this is j minus m.

So I can take them together and you see j minus m will cancel here. Similarly, this is j to the power of j and j to the power of j plus s minus 1, so I simplify that. This is j minus m divided by j to the power of s minus 1. So, things have simplified a lot now.

(Refer Slide Time: 15:27)



Probability

$$\text{Probability} = \left(\frac{j-m}{j}\right)^{s-1}$$

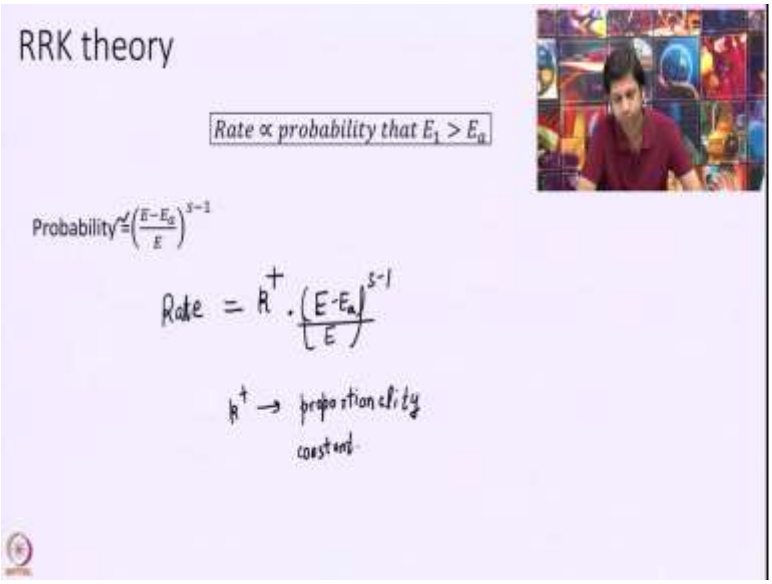
$$= \left(\frac{h\nu j - h\nu m}{h\nu j}\right)^{s-1}$$

$$= \left(\frac{E - E_0}{E}\right)^{s-1}$$

$E = jh\nu$
$E_0 = mh\nu$

Now, we will get back to the language of energies. Remember that energy, the total energy we said is equal to jh nu and E naught is mh nu. So I come back to this equation and I multiply by h nu in the numerator and in the denominator. So, h nu j is nothing but e, h nu m is nothing but E naught, E.

(Refer Slide Time: 16:07)



RRK theory

Rate ∝ probability that $E_1 > E_a$

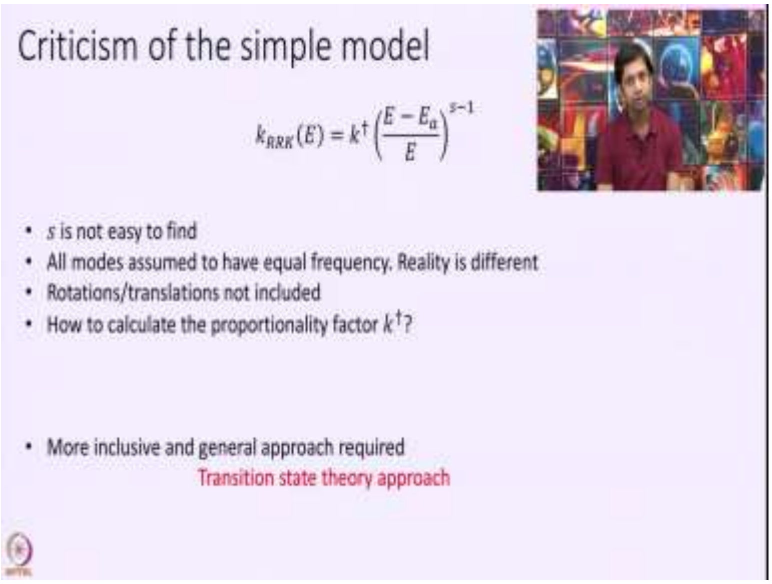
$$\text{Probability} \cong \left(\frac{E-E_a}{E}\right)^{s-1}$$

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

k^{+} → proportionality constant

So, finally, remember that the rate is considered proportional to the probability that E1 is greater than Ea and that probability we have shown to be approximately equal to this E minus Ea over E to the power of s minus 1. So, the rate is then proportional to this probability. So I put some proportionality factor, sorry, where k dagger is a proportionality constant.

(Refer Slide Time: 16:58)



Criticism of the simple model

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

- s is not easy to find
- All modes assumed to have equal frequency. Reality is different
- Rotations/translations not included
- How to calculate the proportionality factor $k^{\dagger}$?

- More inclusive and general approach required

Transition state theory approach

So, this is really a very, very simple model. This was came in 1920s and it is not very well used today, but it is still very instructional. It is instructional because when you do science, what you do is to really come up with the simplest possible model that you can think of. Real life is extremely complex and modeling it directly is extremely hard. And so this is how we always begin. We always begin with simpler models.

And if that does not work, then we will better models. So I wanted to show you this model, so that you know how models evolve. We do not come up with the complex models out of the blue. We come up with building simpler models and developing over them. So this model, of course, has a lot of problems. First of all, for a real molecule, a real system what is s exactly? Not easy, not easy to tell. Second, we just said that all modes have equal frequency.

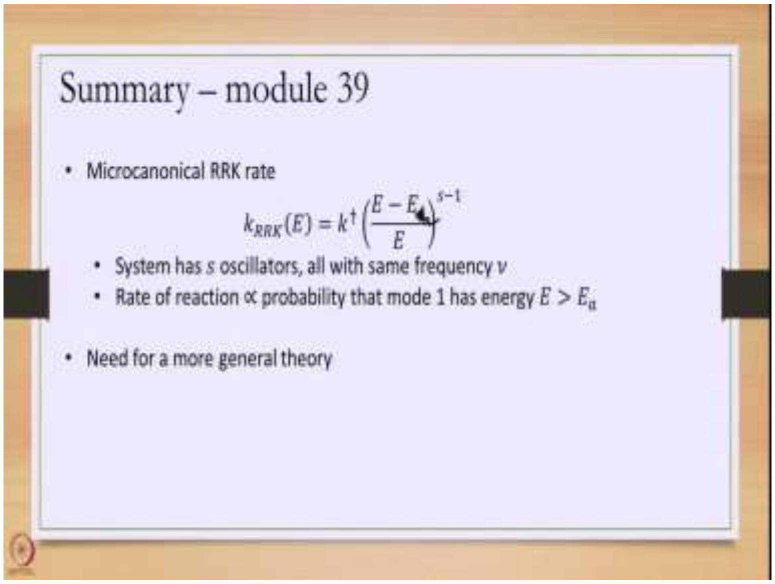
You must be shouting out at me by now. How can I possibly assume that index of course is bad assumption? You think of water molecule. The two bends are like 200 or 300 wave number and one stretch is 2000 wave numbers. Any spectroscopist will tell you that there is a huge variation in different frequencies. So, of course, that is a bad approximation.

What happened to rotations and translations? I completely forgot about them, did not I? That have also be included. Remember that transition state theory at canonical ensemble, we did rotation partition function too and that plays a big role. We do not have that here. We have simply vibrations. We just started saying we have a harmonic oscillators, but that can be questioned as well.

And finally, I just introduced this factor at the end and said there is a proportionality factor k dagger. Again, you must be screaming what are you doing? How do I calculate this k dagger? It is actually in, within this model it cannot be calculated. It simply a parameter. So this is really a simple model and we need a more inclusive and general approach and that approach come from transition state theory.

So, remember this came in 1927 and '28. Transition state theory came in 1935. So after 1935 in transition state theory in canonical ensemble when that was developed, then people use that theory to build upon constant energy version as well. That was done by Marcus in the 1950s, I believe, I will have to double check once more. And that is what we are going to discuss in next modules.

(Refer Slide Time: 19:54)



Summary – module 39

- Microcanonical RRK rate

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

  - System has s oscillators, all with same frequency ν
  - Rate of reaction ∝ probability that mode 1 has energy $E > E_a$
- Need for a more general theory

So today what we have discussed is very simple model, the RRK model, to calculate rate constant at constant energy. Within this model, we derive rate constant as k dagger into E minus Ea over E to the power of s minus 1. And the model, the important approximations that we make is that the system has s oscillators all with the same frequency nu and the rate, this rate was estimated as the proportional to probability that mode 1 gets energy more than Ea. This one I have capitalized, let me make it small. That is a typo.

And along the way we made one more approximation that we have large energy E is much, much greater than Ea and much greater than s minus 1 actually. So j minus m is much, much greater than s. But we need a more general theory that we will develop in next module. Thank you very much.