Chemical Kinetics and Transition State Theory
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Lecture 38
Microcanonical rate constant: putting balls in jars

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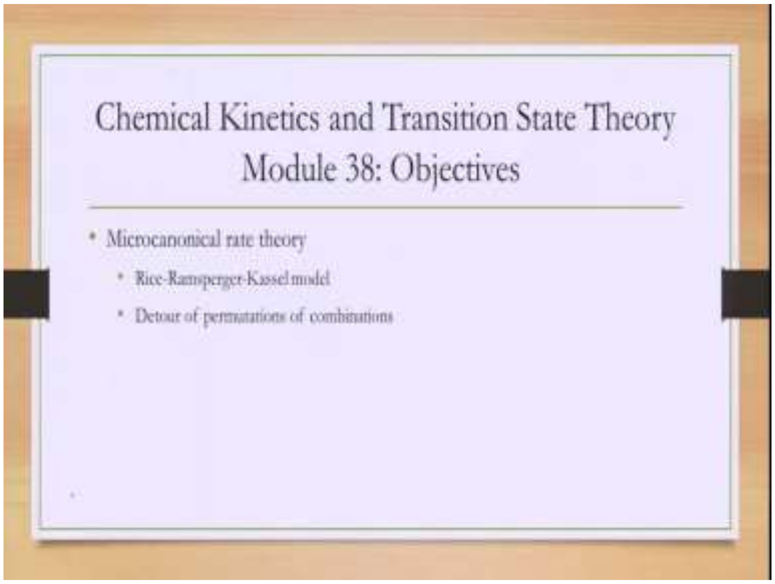

Hello, and welcome to module 38 of Chemical Kinetics and Transition State Theory. In the remaining modules, we will switch gears a little bit and discuss the last leg of this course. What we will discuss now is calculating rate constant at constant energy so in a different ensemble. So far we have been looking at how to calculate rate constant at a given temperature.

But let us say there is no bath, we have a constant energy simulation instead, constant energy system instead, how to calculate rate constants. We will start today with a rather simple treatment done by these three gentlemen, Rice, Ramsperger and Kassel in 1920s. And today we will interestingly take a little detour of permutations and combinations.

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So what I am teaching today, you can find in this book by Steinfeld, Francisco and Hase in Chapter 11.5. I have also given to the more interested readers the very original papers that were given in 1920s by, one by Rice and Ramsperger and the other by Kassel.

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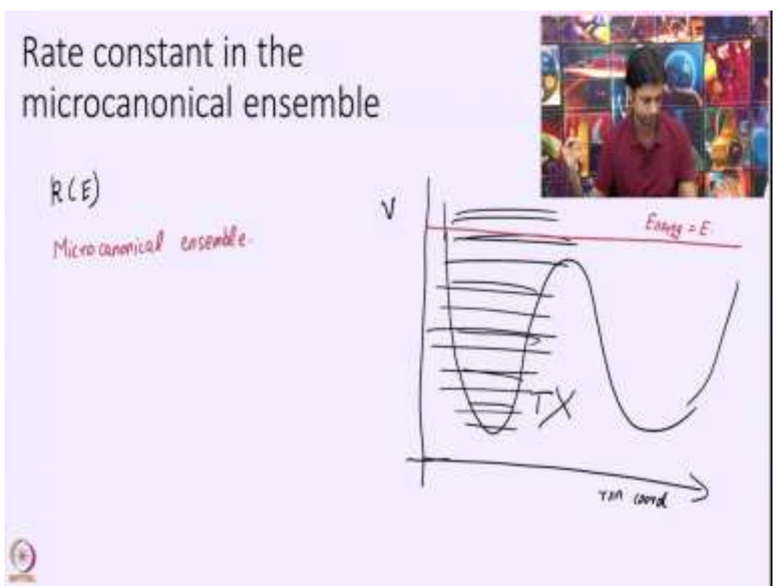

So first let me be clear on what our goal is. We are trying to find the rate at a given energy. So, again, I like drawing 1D surfaces. So this is some kind of a potential energy surface that we have drawn many, many times. So far we were working at a constant temperature, which means you have an ensemble of states. So this was net constant temperature. Now, we will fix one energy here. Let me just use a different color. So that this comes out well in color red.

So if I am at this given energy instead not at a temperature, what, how do I calculate rate constant that will be the focus now. So this is called a microcanonical ensemble. So far what we were discussing was the canonical ensemble which was at a given temperature.

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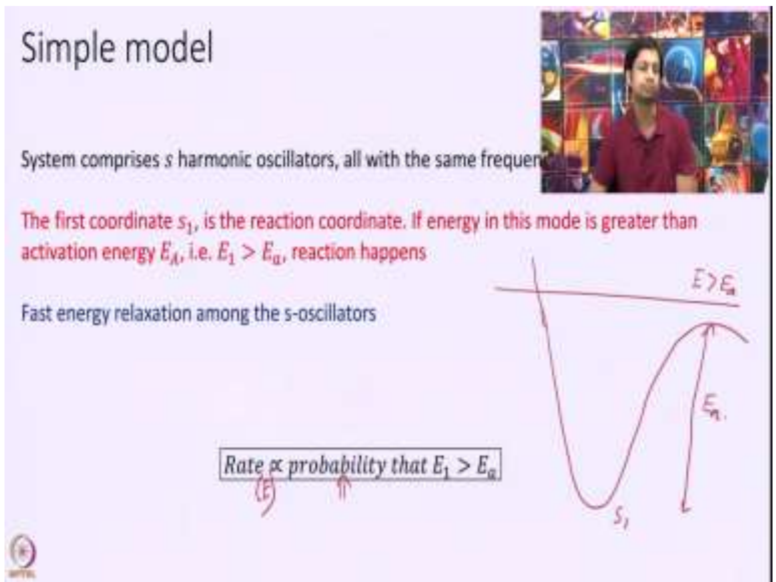

So let us proceed. What I am presenting you today is somewhat instructional, today and tomorrow. This looks at a very, very simple model. This model was developed by these three gentlemen, Rice, Ramsperger and Kassel in 1927 and ‘28. So let us go through this model and let us see what we learn from this. So our model consists of just imagine s harmonic oscillators. So these s harmonic oscillators essentially refers to s let us say vibrations in the molecule.

So I have s vibration somewhere in the molecule. And for simplicity, we are going to assume all have the same frequency nu. The next point in the model is that we have one particular harmonic oscillator, let us call that one to be s1, that coordinate represents the reaction coordinate. So, therefore, if a certain amount of energy gets deposited in this reaction coordinate, the reaction will happen. So I have total energy E, sorry, I want the pen.

So this is my mode s1. I am thinking of it as harmonic oscillator, although I have drawn a little curve here. So this is essentially representing Ea. So if I get energy in this one mode greater than

Ea, my reaction will happen. So the final thing we are going to assume is that there is fast energy relaxation among the s oscillators. The consequence of this assumption really is that we can assume everything is equally distributed. So, all modes have equal probability of getting the energy. It is just a matter of permutation and combination.

So the rate of the reaction at a given energy, let me make it absolutely clear, rate as a function of energy will be proportional to the probability that mode one has energy greater than Ea. So this is our essential model. This is our starting point. This model I want to cover not because it is most accurate model, it is not very well used these days. We have a better model which we will discuss post this model.

But my intention of covering this model is to give you a sense on how science works. We always start with the simplest possible model that we can get and this is a simple enough model. And based on that simple model, then we make predictions. And predictions that can be experimentally verified and see how this model test against experiments. If it tests well, then our approximations are good. If it does not, then we better get a better model.

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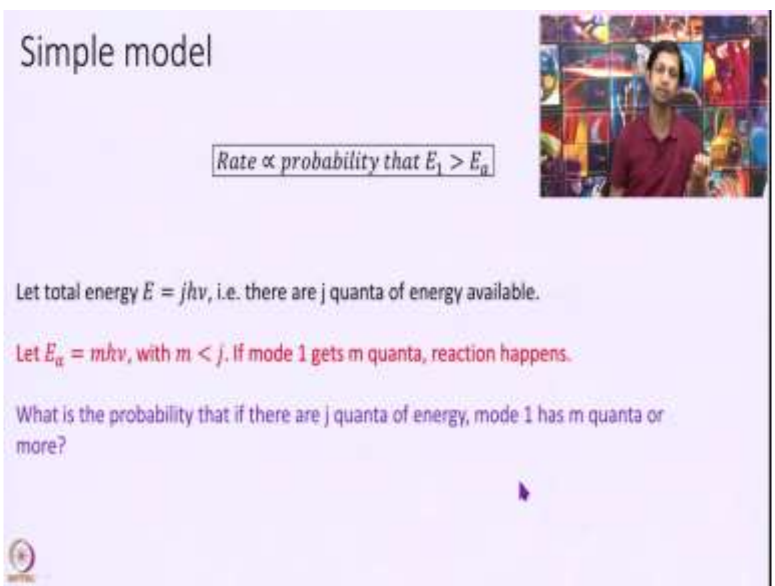

So the rate is now proportional to probability that the mode one energy is greater than Ea. So we are going to assume quantization of energy in harmonic oscillators. So let us assume that the total energy E represents j quanta of energy. Let Ea represents m quanta of energy, where m is of course less than j. So our question is, what is the probability that if there are j quanta of total energy, mode one gets m quanta or more that is what is proportional to the reaction rate.

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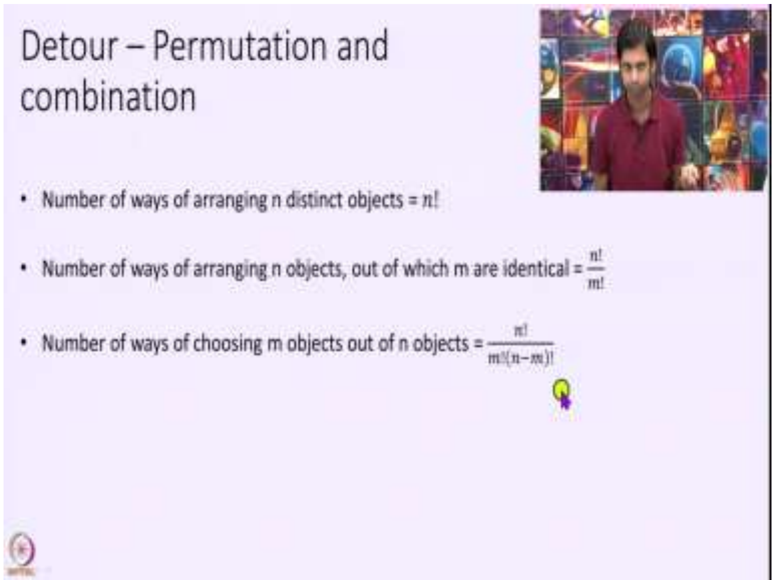

So to calculate this, we will need a little detour of permutations and combinations, something that you have studied in your high school and I think I can easily say, safely say that none of you would have ever thought that this permutations and combinations can possibly be used in chemistry, but here we are. So what we learn you never know when it becomes useful.

So, if your younger colleagues ask you why do they ever teach you permutations and combinations, you tell them to calculate rate constants. So we are going to assume a few principles from our 12th class knowledge of permutations and combinations. I am not going to derive these points. If I give you n distinct objects and I ask you, what is the number of ways of arranging n distinct objects that is n factorial.

So I am simply stating it this is not hard to prove, but we are assuming this to be true. A number of ways of arranging n objects out of which m are identical is given by n factorial over n factorial. In fact, I can generalize this that m1 and m2 are identical. I have two separate groups of m1 objects that are identical and m2 groups that are identical, then what does, what is the answer here, n factorial divided by m1 factorial into m2 factorial.

And finally, number of ways of choosing m objects out of n objects is given by ncm, which is n factorial divided by m factorial into n minus m factorial. We will start out by assuming these three points.

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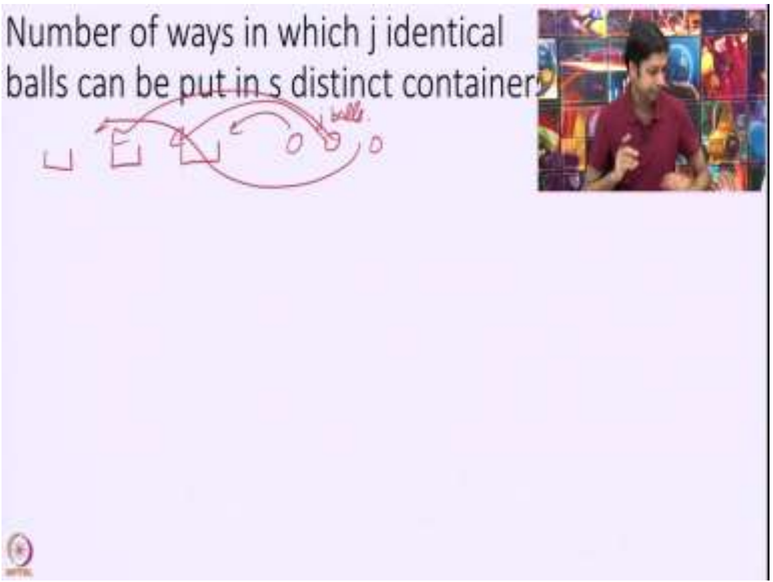

So our main question really is that we start out with some quanta of energy that I will be distributing in my modes. So I will start with a related question that is, that can be built up to answer that probability question we had earlier. What are the number of ways in which j identical balls can be put in s distinct containers?

So I have s distinct containers, sorry, and I have some number of balls with me, j balls. How many ways can I put these balls in these containers? Each container can also have 0 balls, 0 to as many balls as we want to put, but I want the total number of balls to put is j. So this is a little puzzle for. If you like solving these puzzles, you should pause this video. This is a very interesting way to solve these, very, very creative way to solve this actually.

We will solve this right now. If you are interested in solving these kinds of puzzles, which are always fun, pause the video and solve it for yourself, because once you see the solution there is no turning back. When you have seen the solution and that creative answer, you will never be able to come on your own. Somebody told you that creative answer.

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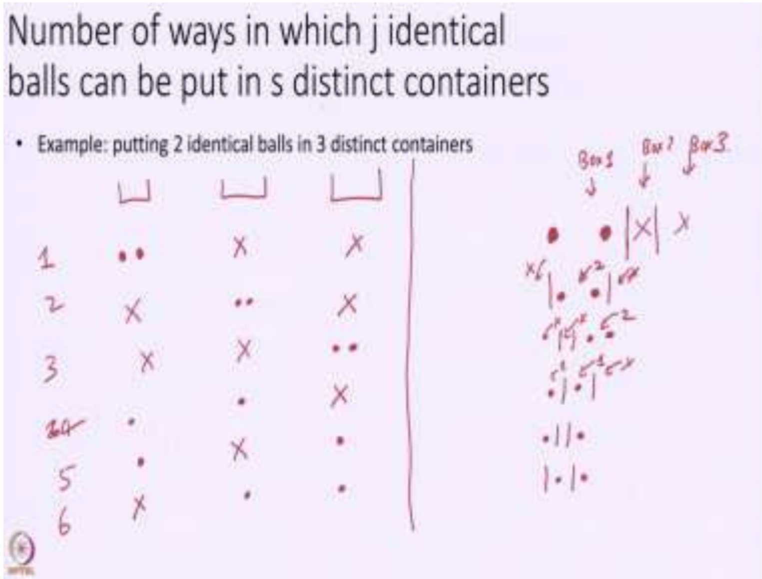

So we will start with an example. Sorry, I over, I will erase this thing. Let us start with an example and start building our intuition on how to solve it for a general problem. Let us assume I have two identical balls that I want to put in three containers. I have container 1, container 2, container 3 and I have two balls I want to put.

So, let us see how many different ways I can put it. I can put both of the balls here and nothing here and nothing here. I can put nothing here like this, my bad, too many balls or I can put both the balls in the third box. Alternatively, I can put one ball here, one ball here, nothing here, one ball here, nothing here, one ball here, nothing here.

So these are all the six possibilities. There are only six ways I can do it. There is no other way I can put these two balls in these three containers, and remember that two walls are identical. So these are only six possibilities. Now, comes the creative part of the solution on how to solve this. I can write these six configurations as a set of balls and sticks.

So, just bear with me. I will draw two balls. I have two balls with me. So I draw two balls here. And I have three containers. So three containers means essentially I have to partition these two balls into three partitions. So to partition it in three ways, I will put two sticks. So let me draw this as these two sticks.

When I draw a configuration like this, this is box 1, this here is box 2 and this here is box 3. So I have put two in box 1, nothing in box 2 and nothing in box 3, which represents configuration number one. Second configuration is given by, I draw two balls, first one has nothing, second one has two and third has nothing. So nothing here, two hear, nothing here.

The third one is this configuration, nothing here, nothing here, two here. Now, fourth configuration, I have one ball, one stick, one ball, one stick. So I have one here, one here, nothing here. Similarly, let me write for the others like this. So, at the end of the day, I can write each configuration alternatively as an arrangement of two balls and 3 minus 1 sticks.

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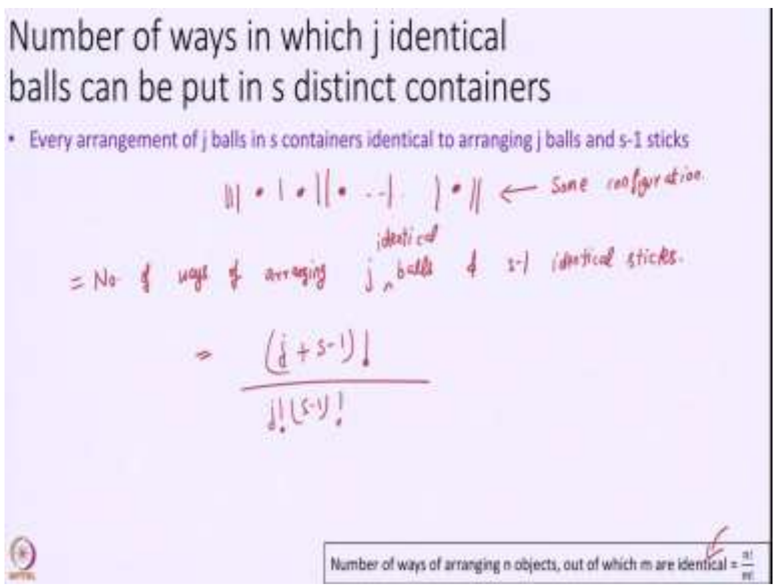

So if I want to generalize this, every arrangement of j balls in s containers is identical to arranging j balls and s minus 1 sticks. So I have j balls with me here now. And if I can put s minus 1 sticks in some fashion here, then this will correspond to some configuration and this configuration is unique. Each arrangement of j balls and s minus 1 sticks corresponds to a unique configuration and all possible configurations can be covered.

So all I have to do is to calculate the number of ways of arranging j balls, j identical balls, let me make it absolutely clear, and s minus 1 identical sticks. So this is, remember, we had already told the answer for arranging n objects out of which m are identical. So we have j plus s minus 1 objects. I have j balls s minus 1 sticks, so total of j plus s minus 1 divided by j are identical and s minus 1 are another group of identical objects. So this is the number of ways in which j identical balls can be put in s distinct containers. It is a very clever trick.

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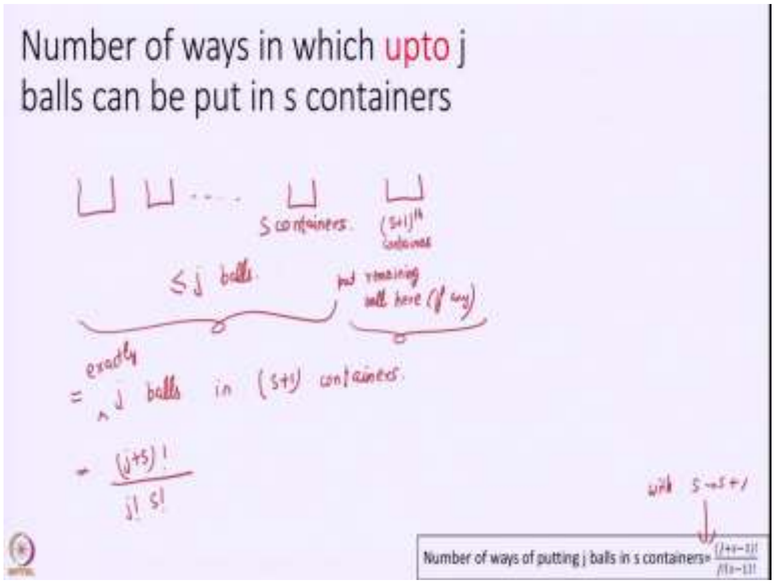

So let us ask another puzzle to you. Given that we have found this number of ways of finding j balls in s containers, now I ask you, can you calculate, my bad, can you calculate the number of ways in which a maximum of j balls can be put in s containers. So, so far we had told that you have to put all j balls into these s containers, none of them have to be left out. Now, let us lift that restriction. Now, I am asking you, you can put 0 balls in these s containers.

You are free to put only one ball among these s containers. You can put up to j balls in these s containers. So how will you calculate that total? Again, if you enjoy solving these puzzles, this is your one chance to solve it, because in a minute, I am going to provide you with an answer, and this is even more beautiful. This is a one line answer.

If you strike the correct thought, the answer can be written in one line. Very simple. You do not have to do anything complex. There are very, very complex ways of solving it. But there is one way of solving it, which is one line answer. So if you are interested pause the video and do it on your own. Otherwise, I am doing it now for you.

So the number of ways in which up to j balls can be put in s containers. Listen closely, it is beautiful. So I have s containers. Now, I have to put up to j balls. So I have less than equal to j balls here. Let us consider one more container and put remaining balls here, if any. So I put let us say only j minus 3 balls here. So I will put the third ball in the s plus 1 container and make it up to j. So whatever is left over, I will put into this s plus 1th container.

So now you see, the problem becomes this number of ways is the ways of putting j balls, exactly j balls in s plus 1 containers. So we just use this formula with replacing s with s plus 1. So this is nothing but j plus s divided by j factorial, s factorial. I told you it is a one line answer.

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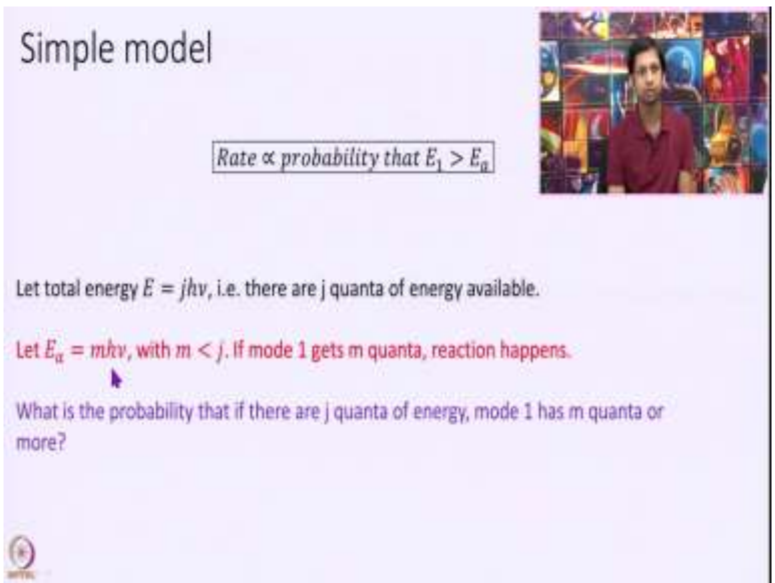

So we have worked a little bit of permutations and combinations today and now we want to apply it to this simple model that we have presented that the rate is proportional to the probability and we have total energy E which is corresponds to j quanta and the first mode if it has more than m quanta of energy, then the reaction happen. So we have to calculate what is the probability of distributing these j quanta among s oscillators such that one of the mode, the first mode has more than or equal to m quanta. So, that we will do in the next module.

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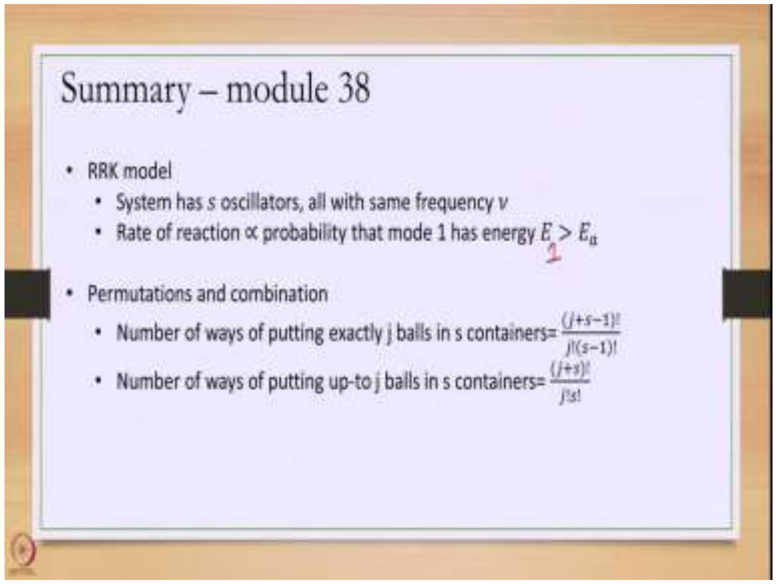

So, today, we have just presented to you the simple model that was developed by RR and K. We usually do not call out their full names, simply call their RRK. It has s oscillators all with the same frequency nu. And the rate of reaction is assumed to be proportional to the probability that mode 1 has energy E greater than Ea. I should put E1 here. And we had looked a, took a little detour of permutations and combinations.

Who knew permutations and combinations is actually useful in chemistry in calculating rate constants. But I hope to convince you that it is. And what we derive today is that the number of ways of putting j balls in s containers is j plus s minus 1 factorial divided by j factorial into s minus 1 factorial and number of ways of putting up to j balls in s containers is given by this. Thank you very much.