Chemical kinetics and transition state theory
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Lecture: 07
Kinetic theory of collisions: initial estimate

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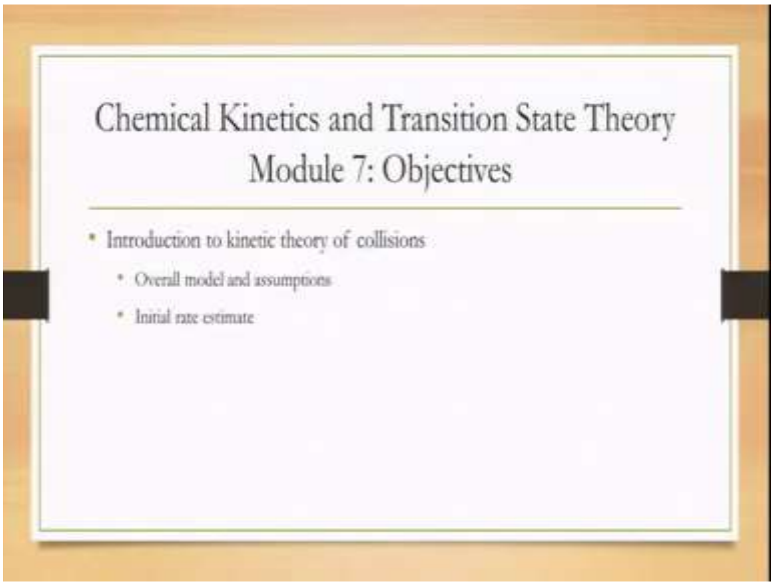

Hello, and welcome to module 7 of Chemical Kinetics and Transition State Theory. Today, we are going to start with one of the important models that is one of the main objectives of this course. We will start looking at kinetic theory of collisions today. A little bit of its history and origins.

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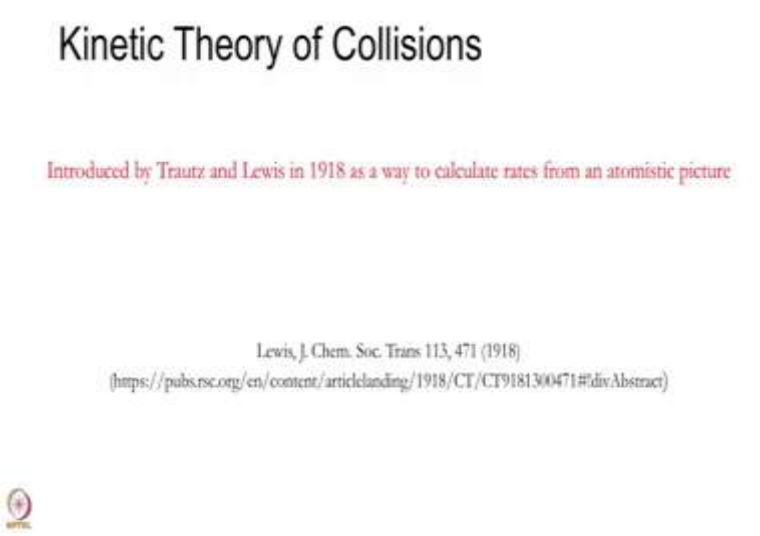

So, it was introduced by Trautz and Lewis in two different papers in 1980. So, this was essentially a build-up over what is the transition state theory, the concept of transition state put forward by Arrhenius. Arrhenius being the genius, he had the vision in late 1800s to postulate that the transition state exists. What he did not provide is how to calculate the rate constant, he gave a formula.

But he did not give how to actually get the parameters that are there in that formula. So, that is what proceeded after our genius, people were trying to figure out. Well, you give me a reaction, and I will try to find out what that rate constant is going to be. And well remember in this time, also, the idea of atoms and molecules were also emerging. Dalton happened only 100 years before that.

So, people had figured out Trautz and Lewis particularly, one way to find his rate constant from an atomistic picture. So, here, I have actually provided you the original paper, you can go at it and look at it; this is a very readable paper, by the way. And, I mean, this is not going to be a part of the syllabus. It is too advanced for that at least.

But if you are interested in this field of chemical kinetics, as general, do read this paper, it is a beautiful paper, and it has a lot of insights. It really shows you how these scientists thought and developed theories. Even if this theory is not the most advanced theory as of now, but nonetheless, it is 100 years before and it is beautiful, how the scientists thought.

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The resources we are following is basically the chapter 4 of the book by Laidler. I have provided you another reference, which is this website. So, you can look at this and this will also has a very, very good description.

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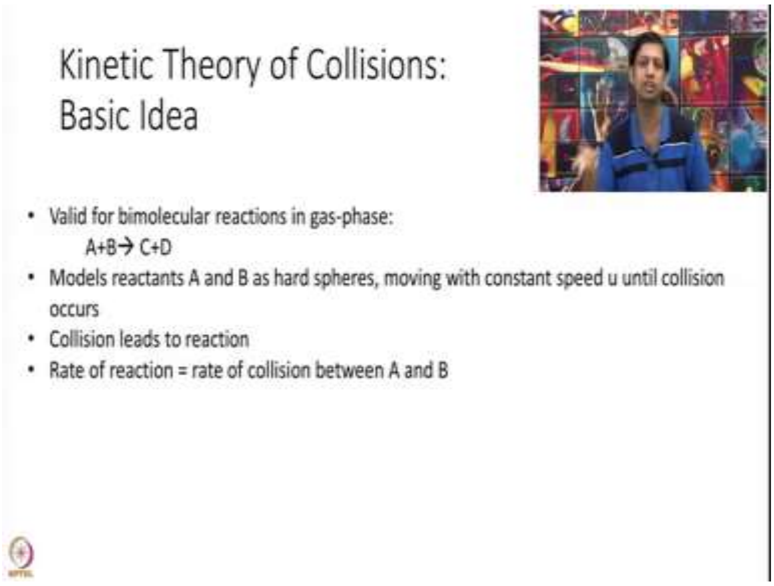

So, let us come to this kinetic theory, and what is the basic idea? What is our model, how are we going to calculate this rate constant? First thing, this model is only for biomolecular reactions, that is there are two reactants A plus B, this is on the elementary step. So, I have A and B they are reacting together to give me some products, products can be as many. The main idea, how this theory thinks is that it thinks of A and B.

As essentially spheres moving around in a box or in some box of some volume V, so I have some box some volume V, some temperature T, and I have these reactants A and B, which are basically spheres in gas face running around. So, what we assume a very simplistic model, we are trying to get the first estimate.

So, we are going to make a lot of approximations, we want to keep the theory as simple as possible, we are going to assume that these A and B move with constant speed some U 1 and U 2 until they collide when they collide the speeds can change and when they collide is the point when the reaction happens. So, we are not going to get into the nitty-gritty of bonding there. This theory, by the way, is before a Schrodinger's equation.

Schrodinger equation is in 1920s, 1925, and '26. This is 1980. So, the idea of bonding is still not very clear in 1980. By the way, people had some idea but not very clear. So, this theory says, let us not get into the nitty-gritty of bonding at all. Let us say this collide and whenever this condition happens, a reaction is going to happen.

And so, the rate of reaction is simply equal to the rate of collisions between A and B. So, we have a very simple model with us. We have simplified the problem a lot. We have provided a way for you to think about this problem.

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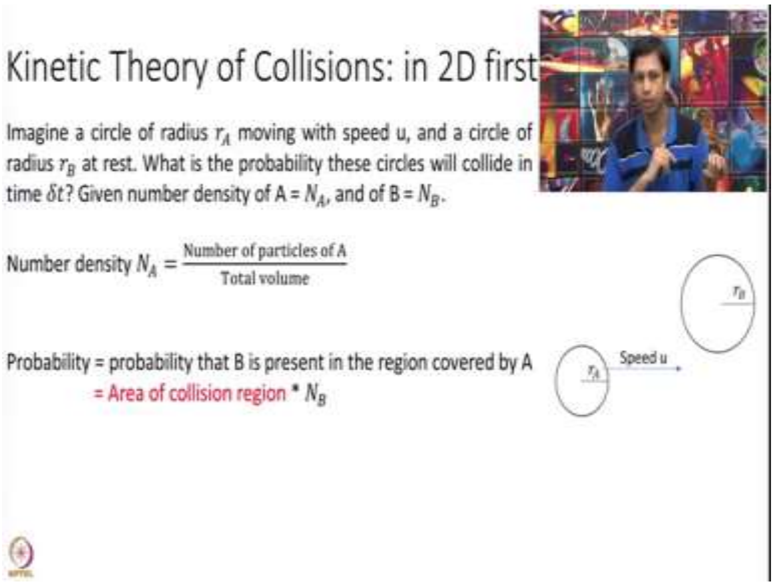

So, let us think, how we are going to calculate, this rate of collisions. To start thinking about it, this problem is, of course, in three dimensions, our world is three dimensional as you see it. To simplify, let us just think in 2-D, just for understanding. So, let us start with a simple question, I want the rate of collisions. But let us ask a simpler question.

Let us say I have a circle of radius R A, it is moving with some speed U, and I have some other circle of radius R B, which is at rest. What is the probability that these circles will collide with each other in some small-time delta T? And let us assume a uniform density of A and B given by N A and N B, where N A is the number density, which is the number of particles of A divided by total volume.

Well, how do I calculate this probability? So, this probability is calculated, well, this probability is equal to the probability that B is present in the region that A covers while it moves, I have small-time delta T, in this small delta T, A will move a little bit forward. So, I have this A, it will move a little bit forward.

And so, it is covering some region. And if B happens to be in that region, well, your collision will happen between these two circles, these two circles will coincide. So, I simplify my problem a little bit further. Now one step more, I say, well, then I find the area that this is A going to cover multiplying by the density of B, that will give me the overall probability.

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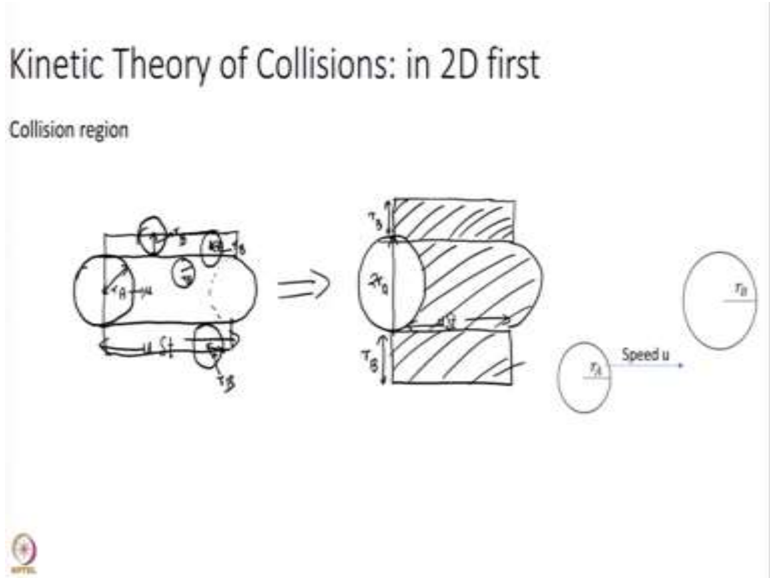

So, I have to calculate this area of this region that A is covering, I call this thing as in general, a collision region. So, let us try to think about this. So, this might not look like a perfect circle to you. But let us imagine it is a circle of some radius R A. So, if I let this circle move forward with speed U in time delta T, how much distance will this circle move? Well, of course, U into delta T. That how you calculate distances.

Well, so if the center of B is inside this. Of course, these two circles will coincide, they will collide with each other. But I want you to note, something more. Even if the center is a little bit outside, let us say my center is somewhere here. You note that (my God, this is at the center) but you can still imagine what I am saying.

Even if the center is a little bit outside, nonetheless, these two circles are still going to collide with each other. Yeah, in fact, I will tell you that the circle can be as far as this when they tangentially touch each other. Any further and these two circles will not touch with each other at all. I can do the same thing on the bottom side as well. So, the point is, that my B can be anywhere, the center of B in this region.

So, let me just redraw this figure. I have A here and I have drawn length of R B here. This is 2 R A that is the diameter of A and this length is U delta T. So, if B is present here, the center of B again. If the center of B is present in this region, which A has moved forward or if B is present here, then these circles will collide. So, I want the area of the shaded region.

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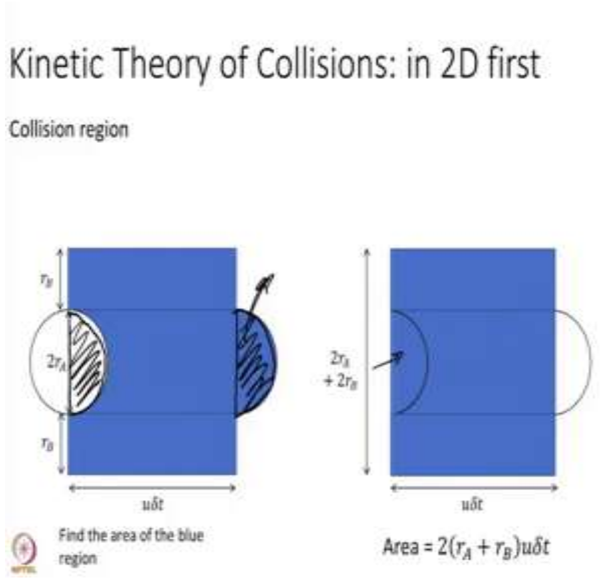

So, a clearer picture is drawn here. And I want the area of this blue region that I have drawn. Take a minute or so and solve this problem. It is a very beautiful problem. It is a puzzle. So, take a minute or two. Think about it, how will you calculate the area of this blue region? So, pause the video and solve this area. So hopefully, you have paused the video and now you are back. Hopefully, you have calculated the area.

If not, please do give it a shot. It is a very beautiful puzzle. How do I solve this? Well, the problem is this semi-spherical region it is hard to calculate this. You can do it a bit more manually, but a simple idea is as follows. You ready for it, it is a beautiful idea. What we do, we take this little region that is here. We take it out, we remove it and we paste it here.

You know that this will fit perfectly here. So, I will get a figure that will look like this. So, I have moved this blue space out and put it in the white space here. Now you see the problem is much simpler, just simply get our rectangle of length U delta T, height 2 into R A plus 2 into R B, which is trivial to find the area. So, it is 2 equals to 2 R A plus R B into U delta T.

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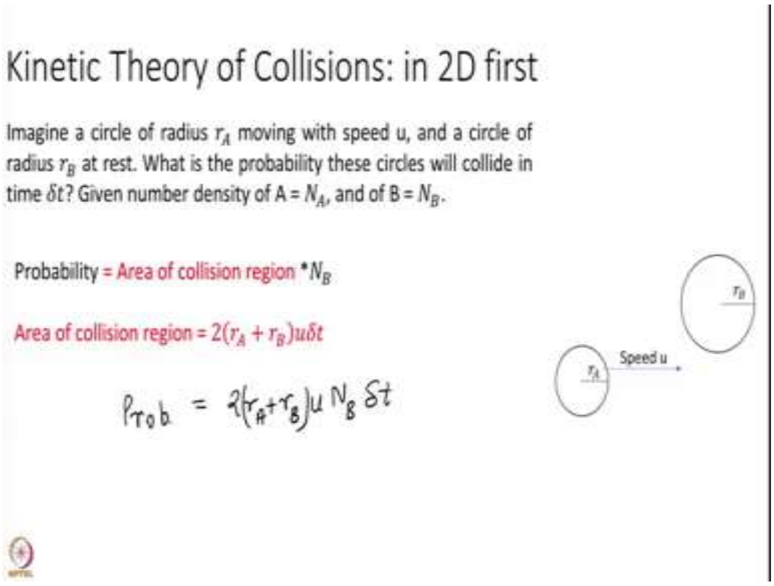

So, I have found the area of collision region, which is 2 into R A plus R B into U delta T. So, now I can get the probability equal to 2 R A plus R B, U, N B delta T.

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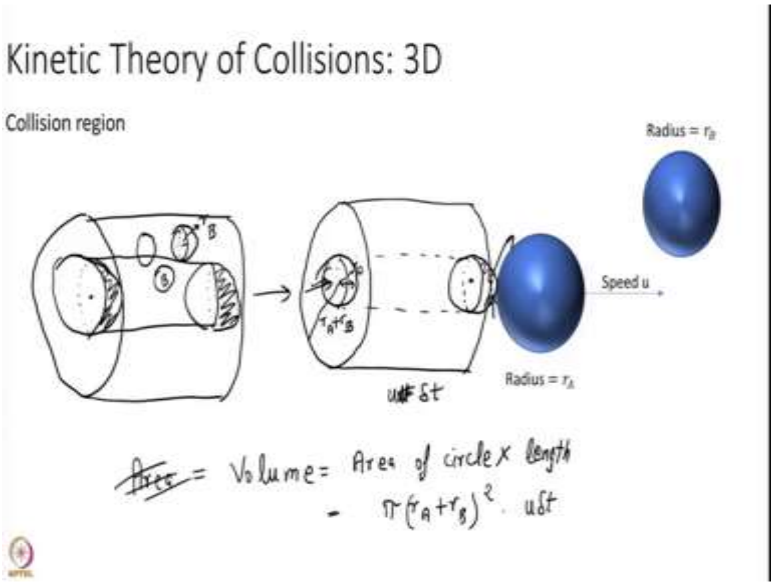

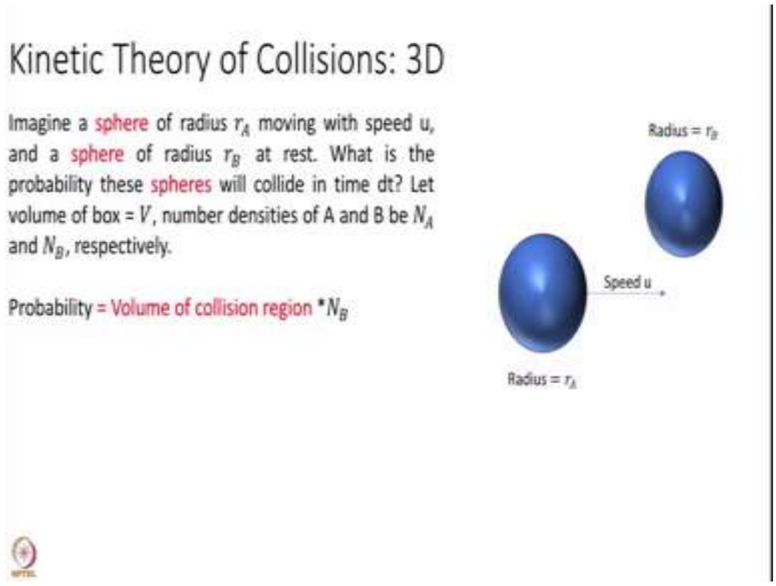

So, that was 2-D, that was just so that we have an understanding of how to calculate these areas and build a basic picture, reality is in 3-D. So, the question remains the same. Now I have a sphere of radius R A made moving with some speed U. And let us assume again B is at rest, we will come to it. Do not worry. I know you have questions. We will come to that. But let us start with assuming B to be at rest, bear with me.

What is the probability that these spheres will collide with each other in some time interval delta T? Again, you can have the number of densities and the total volume is B. Idea is the same, probability will be the volume of coalition region into N B. So again, I have to do the same trick again and find this collision region. Yeah. Now, let us see how good I am drawing it spheres that was my abilities of drawing circles.

So, this is my depiction of a sphere, I will be much more beautiful picture can be found on the right. But the idea is I have a sphere, which is moving forward. Just take circles, the same analog. And well a collision will happen, if B is found inside this region or if B is a little bit outside, B can be here as well, versed conversed, B should be here, so, B is also a sphere.

So, what I get is, essentially a cylindrical looking shape like this and B must fall inside this cylinder. So, let me clean this up a little bit. This is my A. And there is basically this cylinder here. This A had radius R A, while this cylinder has radius R A plus R B, B can be as far as R be outside this region, the center and this is moving forward and I get this cylinder of length U delta T and here is again my A.

So, once more a little bit of A is poking out of the cylinder here, and a little bit of gap is left here. So, we do the same trick there, we take out this patch from here and put it back here, fill it in from the side. So, the area effectively will be the area of this cylinder. So, the area will be, what is the area of a cylinder?

Area of the cylinder is the area of the circle, my bad, I should be using the word volume now, we are in 3-D. So, volume is area of circle into length of cylinder. So, this will be equal to area of circle you all know very well is pi R square. And here R is R A plus R B and the length is U data T, I have used D T, here it should be delta T.

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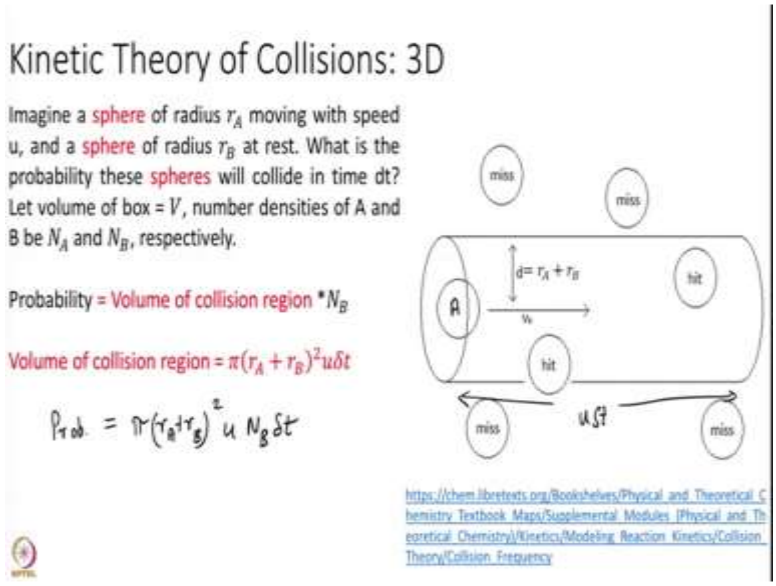

So, a much cleaner picture you can find here, it is taken from this website, this is the same resource I provided earlier. This is my A, it is shown as a circle, and I get this cylinder of size R A plus R B and this length is U delta T. So, if the center of B is inside the cylinder, you have a collision, if it is outside, it is a miss.

And so again like getting back to if the probability is the volume of collision region into N B and volume of collision region we found to be by pi R A plus R B square U delta T. So, I get probability of a collision is equal to pi R A plus R B whole square U, N B, delta T.

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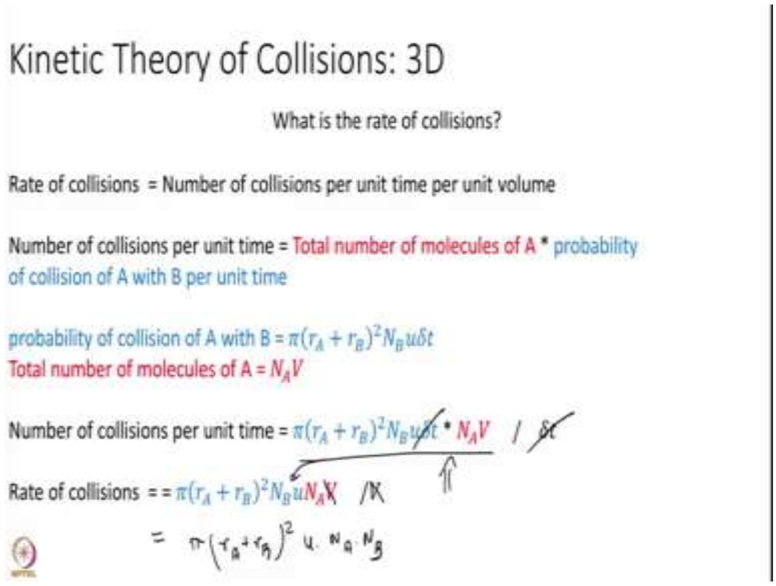

So, what though, we wanted the rate, what am I doing? Why am I calculating these probabilities? It will come helpful. Yeah, I promise you. So, the rate of collisions, by definition is the number of collisions per unit time per unit volume. Remember this, this is how rate is defined of any quantity, what is the number of events happening per unit time per unit volume, every single time for every single thing, anytime anybody asks you rate.

This is what they mean, by the word rate. This is what I have to find. But the number of collisions happening per unit time is the total number of molecules of A that I have multiplied by the probability that A will collide in unit time delta T in this small-time D T, this is their probability finally enters. You see it now.

So, you are convinced that the number of collisions is equal to this, I find the total number of A's and I find. How much if this 1 A is going to collide, what is the probability that this A 1 is going to collide with B? Well, probability of collisions we have already found, and I am just showing you here pi R A plus R B square N B, U D T, this is what we derived.

And the total number of molecules of A is nothing but N A into V, remember N A is the particle density. If I multiplied by V, I get to number of particles. So, the number of collisions per unit time, I multiply these two quantities, and I divided by delta T, this is the total number of collisions, but I wanted to find it per unit time.

So, I divided by delta T. And so, the rate of collisions. Note, that here delta T cancels. And so, the rate of collisions was the number of collisions per unit time, which is here, per unit volume. So, I take this pi, what I get from here, and then divided by volume. So, again volume cancels and I end up with pi R A plus R B whole square U into N A into N B.

So, that is the rate of collisions. That is what you basically get in kinetic theory. This is our model. I know you have still some questions. One is, of course, what is U? As an experimentalist, one would come to me and tell me your reaction; he will not tell me what is the speed. There is also you notice there is no temperature here anywhere.

I was performing the reaction at a given temperature and mix two reagents at some volume and temperature. Temperature is also not present, so something is fishy. And last thing, you also notice that I had assumed B to be stationary and A to be moving. Of course, that is also not true, why should you assume that? So, these questions we will address in the next module.

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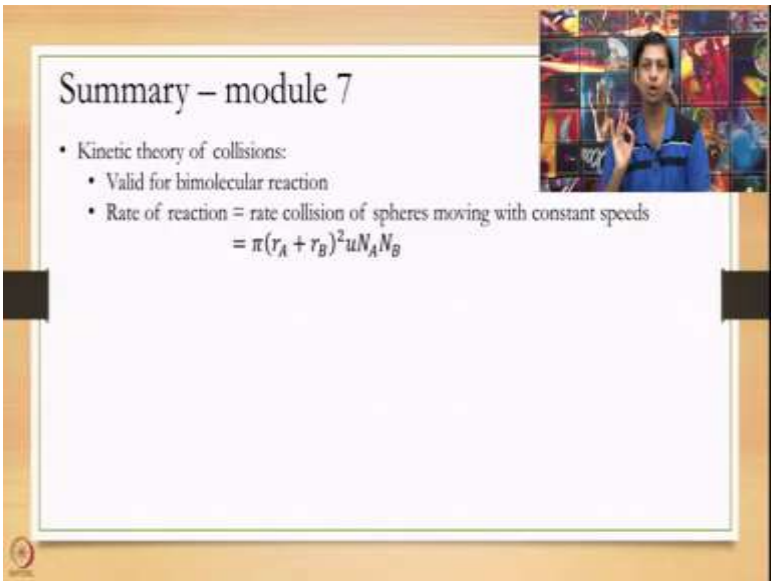

In summary, for today, what we have developed is a very-very simplified idea of how to calculate rate constants, which is called the kinetic theory of collisions. And within this kinetic theory of collisions, the rate is equal to the rate of collisions of two hard spheres of radius R A and R B.

There is no real notion of a bonding here. And what we have shown that if A is moving and B is stationary and A speed is U, this rate of collision is given by the following formula pi R A plus R B square U, N A, N B. In the next module, we will get into more details we will see how temperature enters, we will look into how U is calculated and we will look at how do we include motion of B. Thank you very much.