Chemical kinetics and transition state theory

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Lecture: 08

Boltzmann distribution and kinetic theory of collisions

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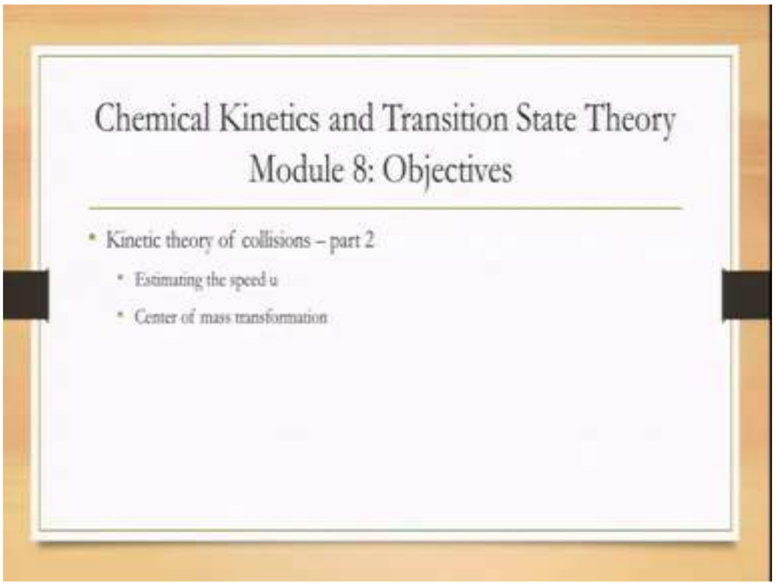

Hello, and welcome to Module 8 of Chemical Kinetics in Transition State Theory. This is a follow up from the previous module, where we introduced the kinetic theory of collisions. So again, our aim is to calculate the rate constant and from an atomistic picture, so that for any general reaction, I will be able to calculate a number out.

In the last module, we had introduced the basic idea; essentially, the rate is equal to the rate of collisions between hard spheres. So, we do not think of any bonds, for now, you think of these reactions as between two spheres colliding with each other. And we calculate the rate of these collisions. We ended up in the last module of the rate as a function of U. And so today we are going to answer the question of how do we calculate this U. And in doing so, we will introduce also the notion of transformation to center of mass.

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So, again the resources for this module, for this entire kinetic theory of collisions is chapter 4 of Laidler's book or you can also look at this link. There also you can see a sufficiently good description.

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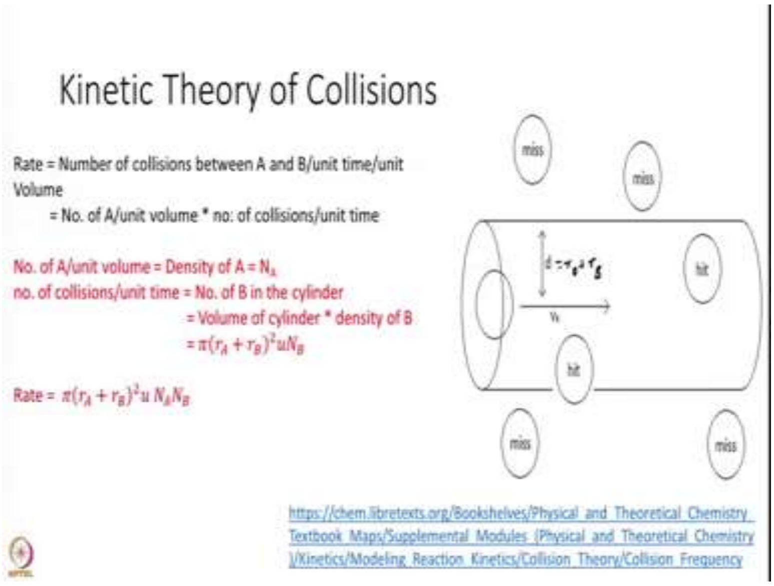

So, just a quick recap, how did we estimate this rate? The rate is the rate of collisions, the rate of collisions is nothing else but by definition, the number of collisions occurring between A and B per unit time per unit volume. This way that I have defined here, and so this I rewrote as the number of a per unit volume into the number of collisions that A has with B per unit time.

Now, number of A per unit volume is simply the density of A, which is N A, and the number of collisions per unit time. We basically estimated, as the coalition region into density of B and the collision region last module, we went into great detail and showed that it is simply this volume of the cylinder that is here where this distance D is nothing but R A plus R B, so we calculate the volume of the cylinder and multiply by the density of B.

That is what we derived in the last module. So, we put this number of collisions per unit time and the density here in this equation above to calculate the overall rate. And that is where we ended in the last module. And so, one very natural question that arises is.

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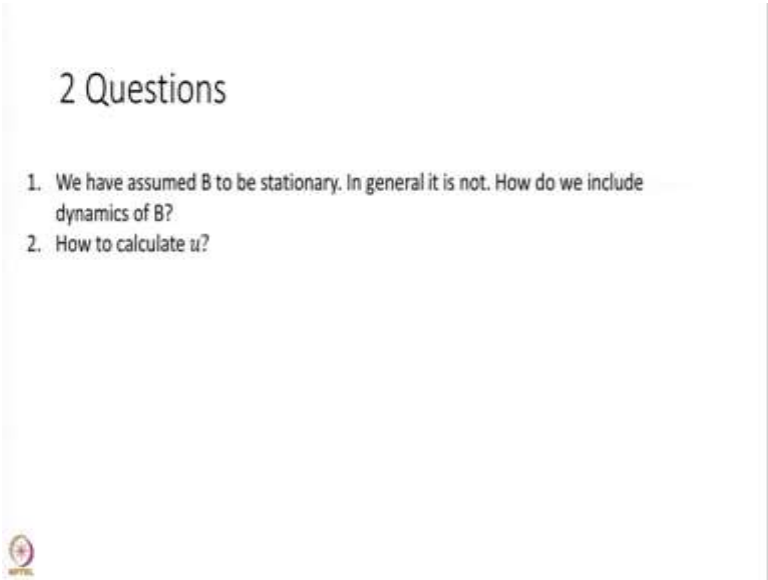

What is this U? Not only this U another assumption we had made while doing this volume calculation is, we assume B to be stationary, what is B is not stationary that that of course is a very ad hoc assumption B is also moving. We are at some constant temperature T and at constant temperature both A and B will be moving. So, how do we account for that? So, let us start with B being not stationary.

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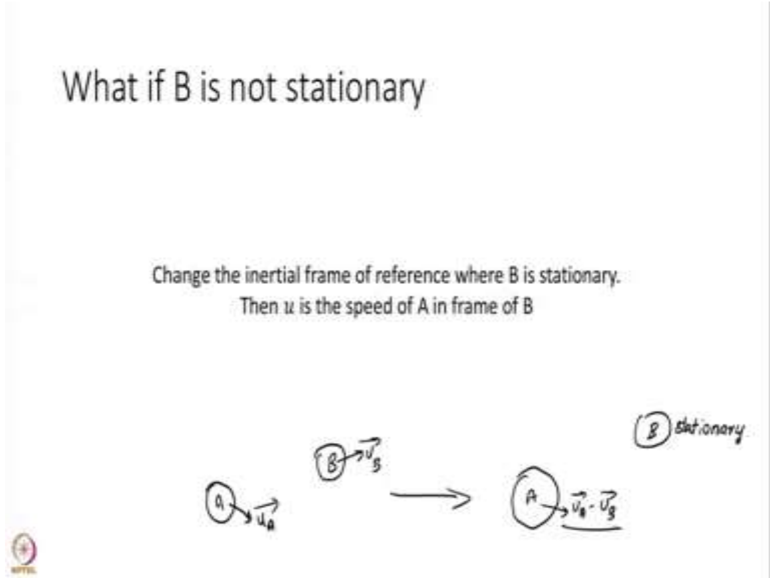

So, let us imagine I have A moving with some velocity UA and B moving with some velocity UB, both are vectors. So, what do I do now? Actually the answer is quite simple. We simply change our inertial frame and go to a frame where D is stationary, we simply change your frame to sit on B. So, we have subtracted UB from every single particle. So, this now becomes some UA minus UB and the B becomes stationary. Yeah, so this U is now this speed essentially.

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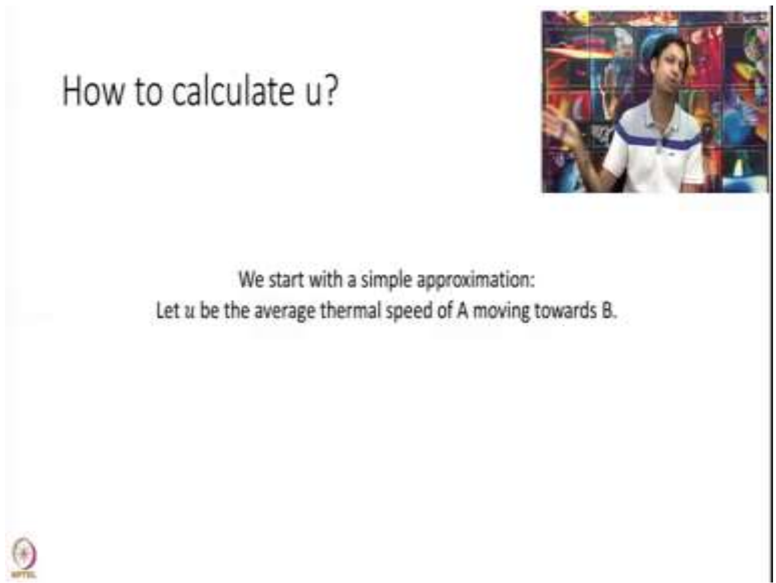

So, how do we calculate this U? So, we start with a very simple approximation, what we do is to pay assume this U to be the average thermal speed of this relative velocity UA minus UB.

So, that, of course, is an approximation, and today we are going to work towards this, but in the next module, we are going to improve upon that as well.

But let us start with this, it is at least a reasonable assumption to start with, we assume all particles are moving with this average speed. And anyway, this whole Kinetic theory of collisions is a very rough estimate. So, it is a ballpark order of calculating the estimate that we are doing. So, that is why we go ahead with this average thermal speed.

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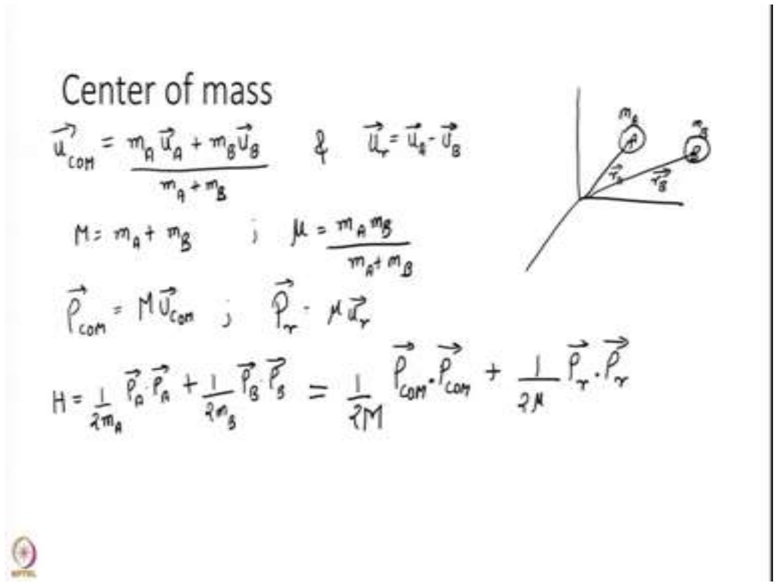

But how do we even calculate this average thermal speed? So, to calculate this average thermal speed, we will have to do some transformations and we go to what is called the center of mass. So, what is the center of mass? So, imagine I have this particle A this is vector R A and I have B and they have their corresponding speeds and momentum. What we do, is we define new variables U center of mass and U relative to be this.

Now, we can also define the corresponding; let us define these total masses as well. So, I define capital M to be MA plus MB and we will need one more quantity, that will soon enough you will see the reason for defining this, this is called a reduced mass. So, effectively define P C O M as M U C O M and P relative as new UR. So, if you have not seen this transformation before it might seem a little bit abstract, but just bear with me.

Soon enough, this will simplify to something very beautiful. And if you have seen this before this will come. For example, if you have studied quantum mechanics of hydrogen atom or even if you study a planetary system, the center of mass is useful, it center of this transformation comes in many-many contexts. The point is, what it will can show is that the Hamiltonian equal to 1 over 2 MA PA dot PA plus 1 over 2 MB PB dot PB.

So, I have my masses MA and MB here. So, this is my neck Hamiltonian. Remember in kinetic theory of collisions, we do not have any potential, my Hamiltonian is simply the kinetic energy that is a very important thing, but you must always remember in kinetic theory of collisions, no potential no bonding. So, this one can show is equal to 1 over 2 M P C O M dot with P C O M plus 1 over 2 mu P R dot with P R. So, if you want you can go ahead and prove this for yourself.

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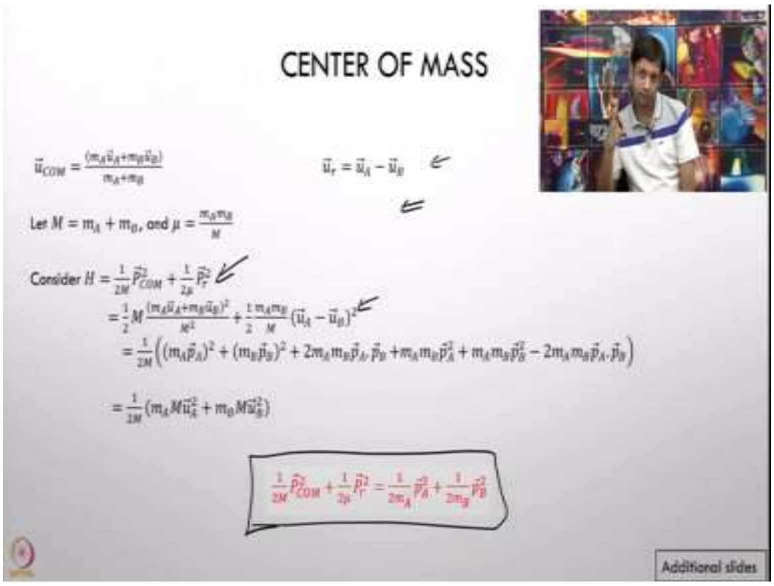

As an additional slide, I have shown the proof here. So, you have to be very careful, it is not hard proof at all. So, you go by the definitions that were defined in the previous slide that I have re-mentioned here. And, you can let us start with this Hamiltonian. This is easier to start with rather than with P A square over 2 MA plus P B square over 2 MB, I substitute P C O M and P R here.

Once you simplify, you will see that sometimes R going to cancel you keep on simplifying, and eventually you will get end up with this. So, this proof is not part of this syllabus, but it is also not hard proof to do, you should be able to do this proof.

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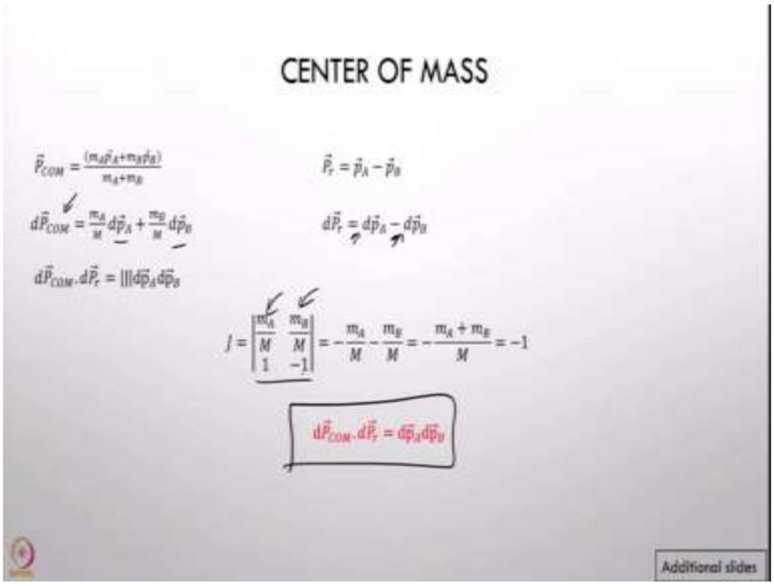

Another point which is going to become important is that the volume element also remains the same. So, you can also show that DPA into DPB equal to DPR into DPC 1. Again, the proof is not part of the syllabus, but I provided you this proof as an additional slide for those who are interested and the proof is very simple. How do you transform?

You essentially, find the Jacobean of the derivative matrix some technical language if you do not know then you can look it up and once you know this language, then it is very easy, all you do is to find the derivative of these variables with respect to PA and PB, you get this MA over MB and B over M and the corresponding coefficients here, you find this determinant and take the magnitude of this determinant. So, these things are easy to prove, although, we will not take this officially as a part of this syllabus.

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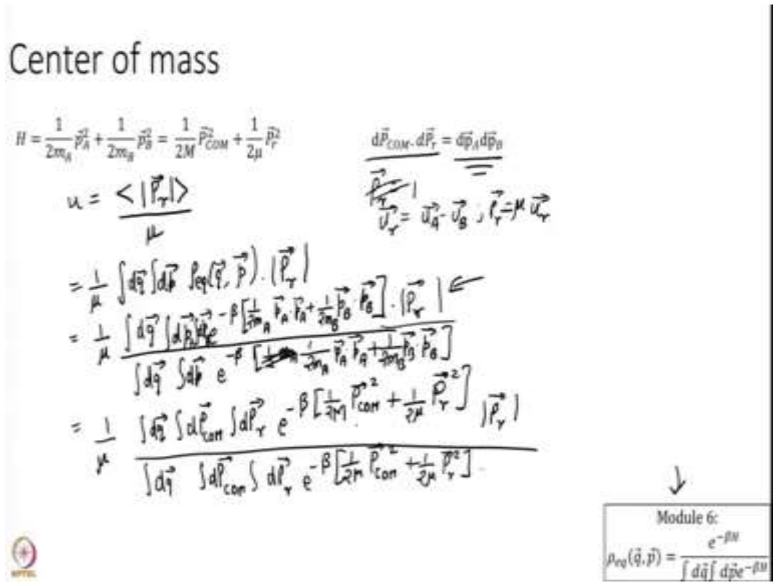

So, what am I doing with all of this? This all mathematics is of course, good. But what is the point? What is the point, is that we are trying to find the average speed? So, let us define this U more formally as this is nothing but the average of this PR by mu. So, that is how we are going to estimate U, it is this relative momentum PR again is my bad, UR again is UA minus UB and PR is nothing but mu UR.

So, PR over mu is your relative speed. And so, this is what we are trying to find, and we are trying to find the magnitude, we do not care about the vector. This relative direction might be moving in any direction across space, I do not care if it is moving up or if it is moving in this direction or towards U. All I care is what is the overall value. So how do we calculate this?

Well, we use our general strategy of how do we find averages, which is equal to 1 over mu, we calculate essentially DQ DP row equilibrium of Q comma P that we looked at a few modules ago, that is also shown here into the quantity that I want to average. Yeah, so I go ahead and I formally put in row equilibrium as E to the power of minus beta H and H is nothing but half 2 MA PA square plus 1 over 2 MB PB square divided by the partition function and you can go back and revise the modules, the partition function is nothing but integral over let me just write otherwise I get confused DQ DP integral over DQ integral over DP to the power of minus beta H. And I have an additional PR in the numerator.

So, now, you see that the separation of H in the language of PR is very useful because I do not know how to integrate this very directly. So, I transform to this center of mass Hamiltonian. DQ I leave aside and remember what is DP. DP is nothing but integral over all momentums which is integral over DPA integral over DPA.

So, I could have written here DPA integral over DPB. But you note that integral over DPA into integral of DPB is nothing but integral of DP C O M into integral of DPI. So, this thing instead, let me erase and I can write that as DP C O M, D P R and the Hamiltonian as well I can write as P R square.

All divided by the same thing, these are vectors, you understand that and here also I have transformed to P C O M and P R, I write the same big Hamiltonian here. So, now, what do you notice that my integral here has neatly separated into the center of mass component and the relative component. So, that is what helps us in simplifying.

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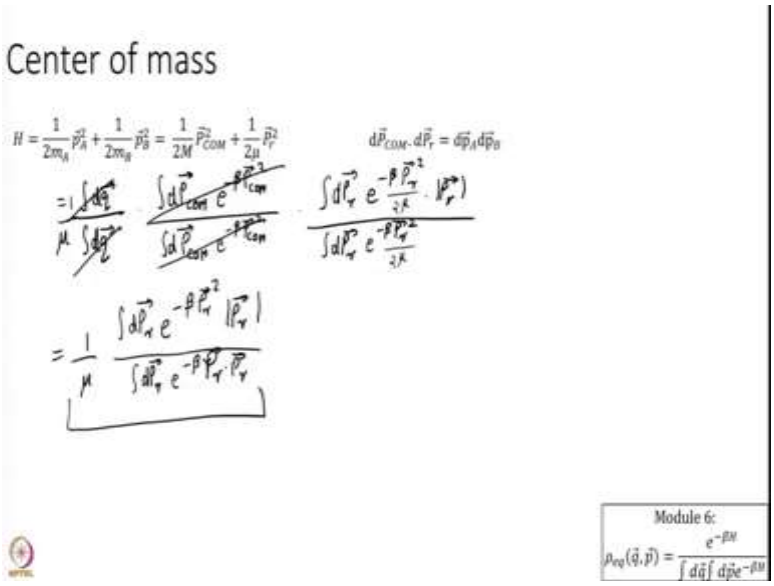

So, the last integral that I have written now, I can simplify that as integral over DQ divided by integral over DQ. So, you can go back one slide and you will note that there is no Q term at all in the integral, multiplied by the center of mass also will very nicely separate out and finally, we have the relative term.

So, I am just simplifying what I had written in the last slide into different terms. So, this portion cancels and I am left with, I have forgotten 1 over mu, 1 over mu DPR beta PR square absolute value of PR divided by DPR, PR square. But, do you recall this term at all, have we calculated this before does it tell you, reminds you of anything.

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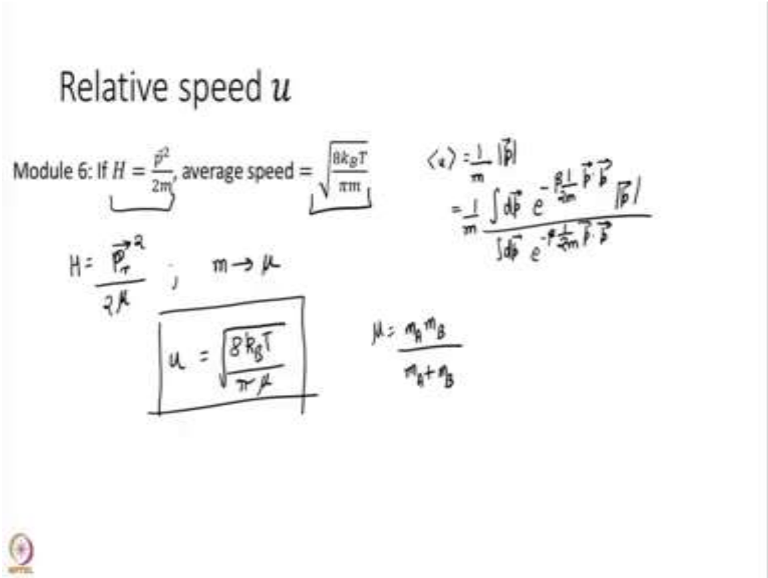

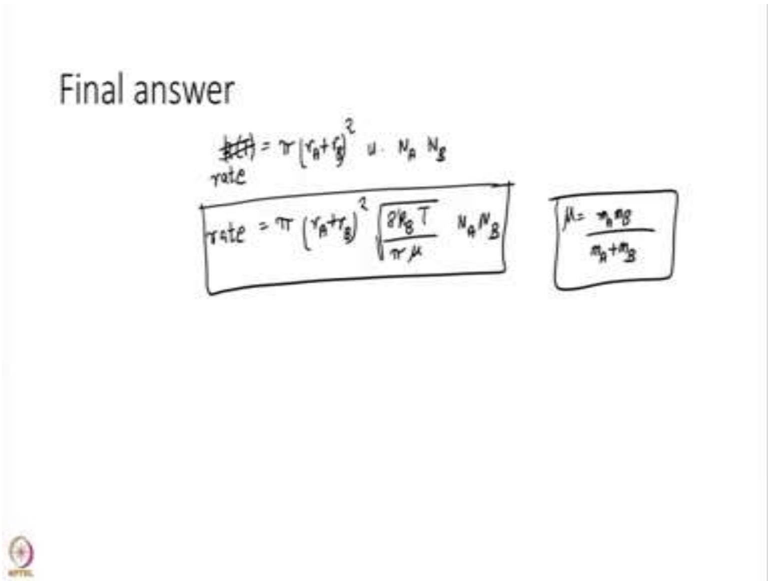

This is nothing but the relative speed. So, remember if we look at just the kinetic energy component before. And for this, we were trying to find the average speed and we define the average speed as nothing but 1 over mass into average momentum. And this was nothing but exactly the quantity that was written in the last slide beta 1 over 2 M, P dot P into the absolute value of P, divided by the partition function.

This is how exactly we calculated this. If you do not remember, go back to a couple of models this is module 6. And in that, we had shown that this is how you calculate average speed exactly. And we showed that this average speed comes out to be root eight KT over pi M. So, I am not going to re-derive it, you can just look back into your model 6.

The only difference in our current R Hamiltonian is, that R Hamiltonian looks like this PR square divided by 2 mu. So, the only thing is here my M gets replaced with mu. So, U in short becomes 8 KT over pi mu, that is your average thermal speed where mu again is called the relative mass. K of T was pi RA plus RB whole square.

I am sorry, this is the rate U into NA into NB and this becomes equal to pi RA plus RB whole square root 8 KT over pi mu NA NB. Where are again mu is and just writing it again so that you have the final answer at one place. So, that is how you calculate rate in kinetic theory of positions at least the first estimate we are going to define upon it.

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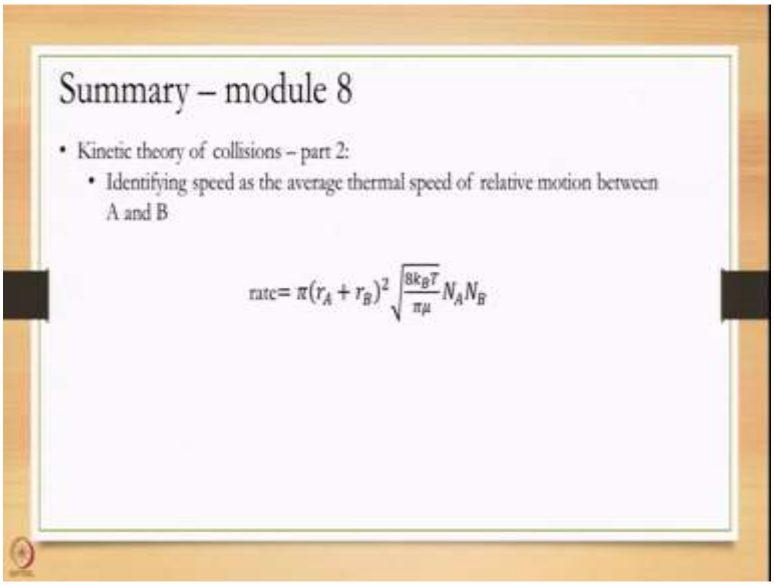

So, in summary for today's module, we have looked at how to calculate this U and we have identified this U as the average thermal speed of the relative motion between A and B. So, we have calculated that formula by doing the center of mass transformation and in that basically, my mathematics simplifies a little bit and I can calculate this relative speed U and with that way, I get the final answer as this rate equal to pi RA plus RB square into this average thermal speed into NA into NB. So, in the next module, we are going to continue from this point, we are going to calculate the rate constant and discuss a few of its properties. Thank you.