Chemical Kinetics and Transition State Theory

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Lecture - 10

Kinetic theory of collisions: reactive cross section

Hello and welcome to module 10 of Chemical Kinetics and Transition State Theory. So, what we are discussing in several last modules is the collision theory, and we are trying to calculate a rate constant. In the last module what we had covered is the comparison of the rate constant calculated from collision theory versus Arrhenius equation.

And we noticed one very important thing that the collision theory is missing the exponential factor itself; that is the Holy Grail. That is what we really really want, that is what made Arrhenius that famous. So, today we are going to see how do we get that exponential factor in collision theory. This concept is basically called reactive cross section that we will be looking at today; so quick recap.

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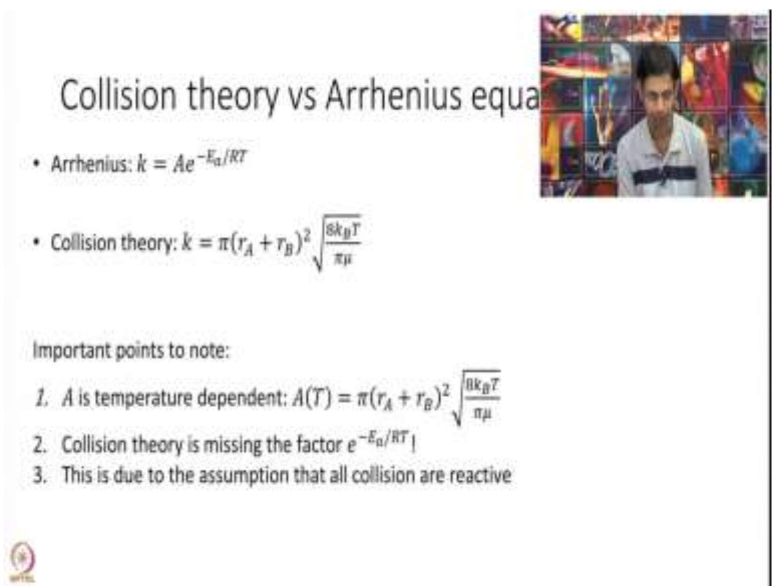

The Arrhenius equation is k equal to Ae to the power of minus Ea over RT, with collision theory what we have derived so far is this equation here. What you noticed that this thing although is temperature dependent, but it does not have this exponential. So, this thing is essentially your pre exponential; this is actually the A of Arrhenius equation.

So, what we noticed that A is temperature dependent; A depends as this square root of T. And we are missing this E to the power of minus Ea over RT. What we will show today the reason we missed this exponential factor is the cause so far we have assumed that all collisions are reactive. Every time A and B will collide, you will get a reaction. So, today we are going to move beyond that approximation.

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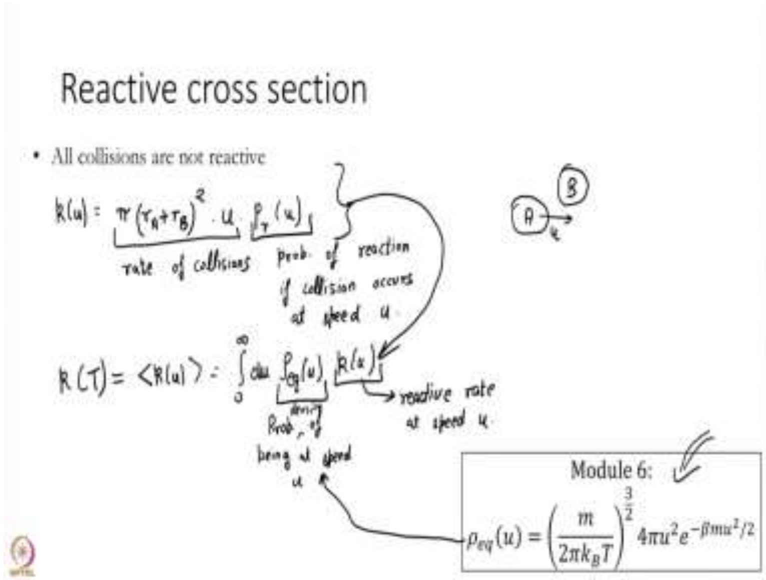

So, how do we account for non reactive collisions that is the question; so, let us start, the way we do it is as follows. First, think of this A moving forward with some velocity u colliding with B; that is how we derive this whole collision theory. And we had approximated u as the average thermal speed; today we are going to do something more accurate.

So, we will start with our basics, we are going to write k of u equal to Pi rA plus rB square into u; so, this is the equation we have derived the three modules earlier. You are that if you are moving that speed u, what is your rate of collisions, correct? We are not going to write away write u equal to root 8 kt over Pi n; we are going to do something better.

Before doing that though we are going to add an additional factor, which is going to improve which is going to get our Arrhenius factor; which is Pr of u. So, this factor was rate of collisions at speed u, and this thing is the probability of reaction if collision occurs at speed u. So, what we are saying is we are having these many collision per second at the speed u; but not all these collisions are reactive.

Some of the collisions just A and B will collide and it will remain A and B, nothing happens; so we are attaching a probability. We are saying that at any given speed u, you have a probability of reacting. At the end though what we are interested in is rate at a given temperature; so how do we calculate that. This essentially is then a thermal average of k of u; so what we do is so well the idea is you have rho equilibrium of u.

This is the probability of will probability density to u more accurate of being at speed u; and this is the reactive rate at speed u. So, I am I am at a given speed, there are two questions: what is the probability that I am at given that given speed u, multiplied by what is the probability that I will have a reaction; what is the rate having a reaction at that speed u.

So, if I multiplied that and integrate to over all speeds; I will get the net rate at that temperature T. And again rho equilibrium of u we derived the few modules are here, is I have just reminding you we derived this equal to this. So, we substitute this big equation here, and we substitute this equation here.

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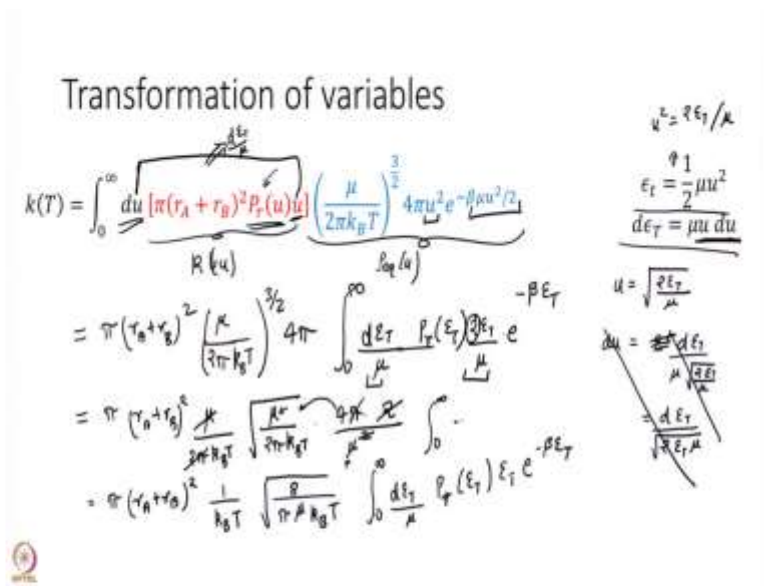

This is your k of u and this is your rho equilibrium of u; I have just written it down, multiplied them together and I have to integrate from 0 to infinity. Always remember the limits of speed is 0 to infinity and not minus infinity to infinity; that is a very very common mistake. Speeds are always positive, there is no such thing as a negative speed in the language mathematics; it is always of absolute value.

Not to make progress I will just make a variable transformation; this is will become very useful; so, I will transform into energy unit rather than speed. And the reason is this probability that is here; it is just much more natural to calculating energy units. Hopefully, that will become clear in a few more slides; so just allow me a few more slides and hopefully just the reason for doing this variable transformation will become clear.

So, I am going to make this transformation of Et equal to half mu u square; I can of course find the differential and I get this. So, I am going to what I am it is a big integral; so I will be very very careful, check carefully if I am making mistakes or not so responsibility. So, I will take all the constants and put them outside pi rA plus rB whole square; that is a simply a constant outside the integral. This big joint mu over 2 pi kBT to the power 3 half; I have a 4 Pi as well.

Let me pull all these constants let me pull outside pull pull outside the integral 0 to infinity. First I note du equal to d ET, let me actually note that I have a u here as well; and let me combine u into du here. So, I note u into du is d epsilon T over mu; all the constants I have taken outside. The next factor is Pr and instead of u, I will just write epsilon T; so this is kind of a new function Pr of epsilon T.

It is mathematically not the same, you understand I am what I am doing; I am converting from u to epsilon T. Or the constants I have been taken care off, I have u square and u square is 2 epsilon T over mu, into e to the power of minus beta and I have half mu u square which is nothing but epsilon T. So, I think I have got all the factors right, let me just go over this; I have all these constants here.

Pi rA plus rB square comes here, this mu over 2 Pi kBT comes here and 4 Pi comes here; all the constants are out integral 0 to infinity, u into du becomes dE over mu. I get Pr of epsilon u square is 2 epsilon over mu that is here; and e to the power minus beta half mu u square is epsilon. So, I have got this equation, I will just simplify this little bit more.

So, what I will do is I will note that I have a few extra constants; I will take these outside, so I will get pi rA plus rB square. Let me just rewrite this slightly differently just to simplify into 4 pi. Now, I have a 2 outside divided by mu square, one mu cancels here; I have a 2 pi that cancels with this 2 pi. So, I am left with pi rA plus rB square, 1 over kBT.

Now, you noticed I have a square root of mu here and the mu here; that is 1 over square root of mu. So, that becomes a square root of and what I will do is take 4 inside; so I will get 16 divided by 2 is 8, multiplied by this integral. So, you can just double can check with yourself, whether the all the manipulations are right or not.

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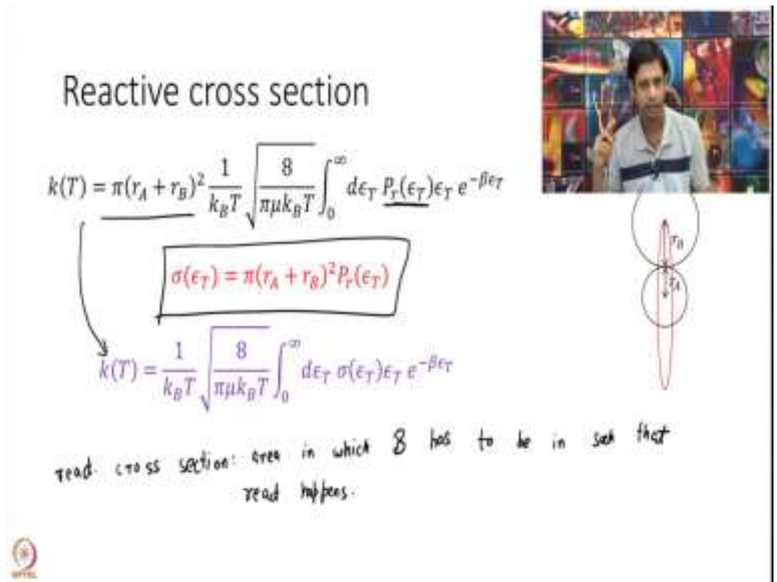

So, after simplifying I get this; it is common actually to take this term here, and multiply by this term. And this is a very important quantity; this is called the reactive cross section. So, I can actually rewrite the same equation here, and write it in the language of reactive cross sections. And what exactly is this reactive cross section? Reactive cross section is the probability is not the probability I am sorry; it is the area that the particle B has to be in such that a reaction happens.

So, I have A moving with some velocity u what is the area in which B has to be in, so such that reaction happens. So, this reactive cross section area in which B has to be in such that reaction happens. So, far we have been assuming that area to be pi rA plus rB square; that is what we have derived earlier; so we have been assuming Pr is 1.

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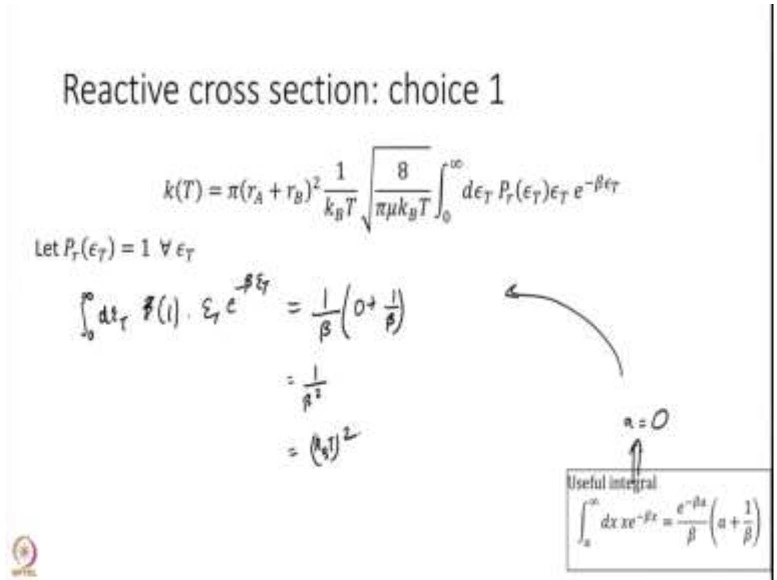

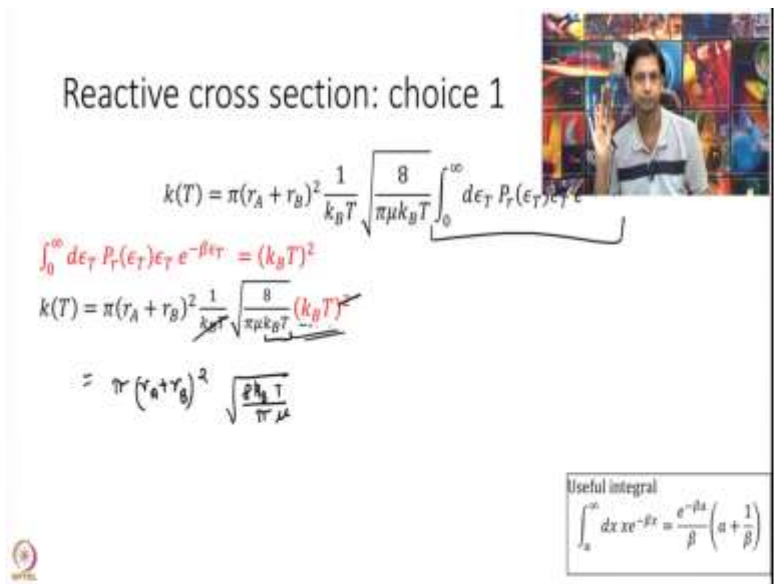

So, now we are going to go ahead and make more sophisticated choices; but first let me convince you that if I choose Pr to be simply 1. What happens? I should get the old result back, what I have derived in the last module; so let us prove that. So, let us assume Pr of epsilon is always 1 for all epsilon; so I have to solve this integral, now Pr is simply 1.

So, this integral I have provided you, here in this integral note that a is equal to 0; so I just copy from this integral here. As a is 0, so e to the power minus beta a is 1; so I have 1 over beta into a is 0 plus 1 over beta; which is 1 over beta square which is nothing but kBT square. So, I take this kBT square and I substitute it in the above equation in this integral.

So, I have taken this and substitute it in kBT square and then I simplify a little bit; and you noticed that one of the kBT will cancel. And you noticed that but they have a square root kT here and a full kT here; so I can write this as 8 kBT over pi. So, you can go back a couple of last module and you will see this is exactly what we have derived. So, this convinces us that the choice Pr equal to 1 is our old choice.

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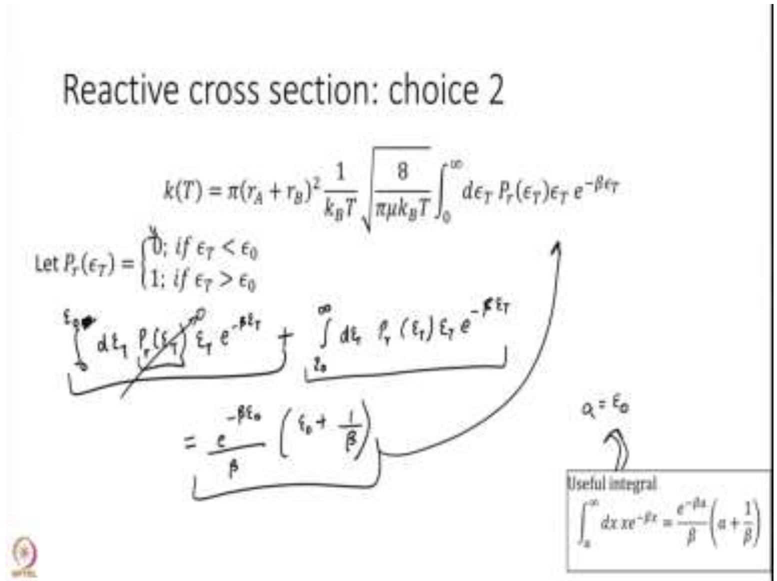

So let us make better choice now. That choice really does not work because it does not get the exponential; maybe one reasonable choice might be that this reactive probability is 0 up to certain energies. That is the reason we went to this units of energy, the transformation of variables. So, I am saying let us choose Pr to be 0, if energy is low enough; it is below some given energy epsilon naught, which is my activation energy and one above it.

So, if your energy is below this threshold, it will not react; if it is above this threshold, it will react that is a natural choice. So, let us assume that is true, so let us do this integral very quickly. So, this integral what I will do is to break into two components epsilon T, e to the power minus beta ET plus epsilon naught infinity d ET Pr ET ET.

And what you noticed this integral is 0 because Pr is 0 between 0 to epsilon naught by my choice. So, I have to integrate this portion but again I have this integral given here, and here a become equals to epsilon naught, so this is simple. This is e to the power minus beta epsilon naught over beta, epsilon naught plus 1 over beta. So, I take this and substitute here.

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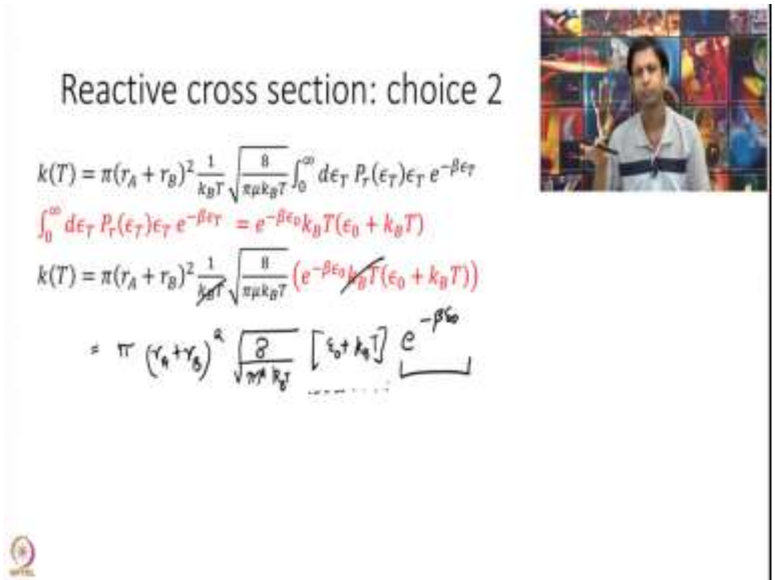

And so I get basically this integral now, this equation. But, you noticed that this is now a much more complex equation; we actually do not end up getting what we expected as a simple Arrhenius equation. But, it is still progress because I do get Arrhenius factor here; but we I get something that is a bit awkward. It does not looks right, this is and actually experimentally also this is not right.

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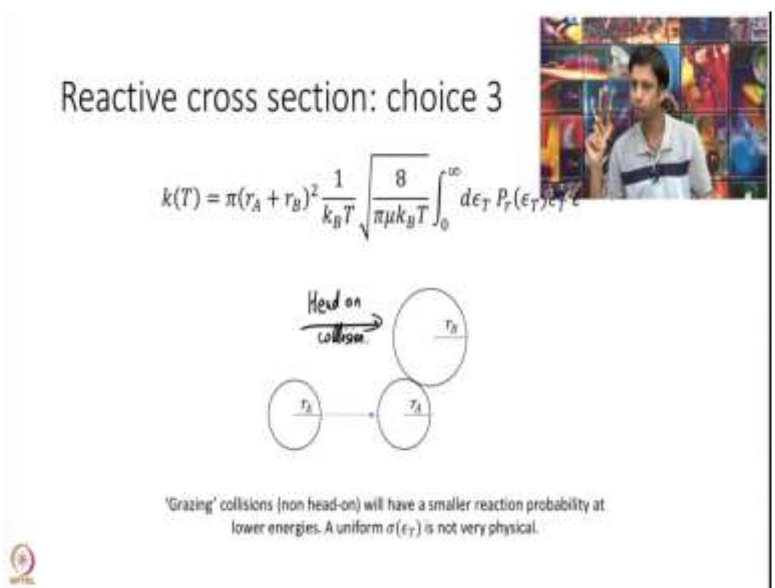

But, we have the reason is that we have made one mistake; we have said that the probability is 1 if your epsilon is above some epsilon naught. But, this is not very physical because I have these collisions happening; sometimes these collisions might be a very grazing collision here. It is array is just it is coming and just touching here like this. And some collisions might be a very head-on collision; so we have not actually accounted for that correctly.

Imagine if you are at some energy; energy basically translational energy, basically it specifies speed. But, at a given speed it is not so obvious, it is not one or zero; because if this particle was coming on head-on. Then the probability will be much higher and if it was just grazing through like; then the probability was very small. So, I have two accounts for that and so how do we do that.

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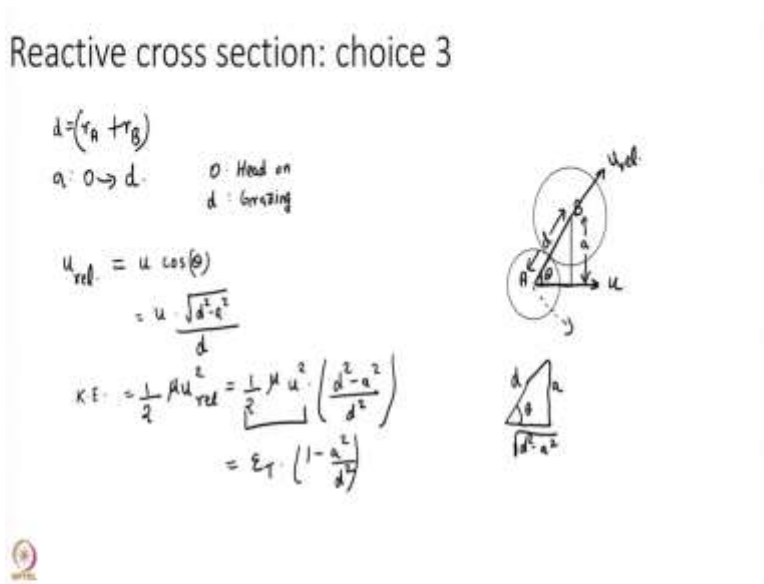

We are going to root trigonometry, so let say I have to get my pen and I keep on forgetting. This is A, this is B and I am moving with some speed u; and it collides here at some angle theta. Let me say this distance is d and let me say this distance is a. We are d is nothing but rA plus rB and a is some parameter that you will soon find out; it should vary from 0 to d. 0 is head-on, d is grazing; so the point is I want to find out u relative.

U relative is the speed along this component; that is the speed I care about. That is that kinetic energy that will be used for reaction. The one that has the perpendicular component plays no role in reaction; that is that is that energy will not be used for reaction. So, u relative, you guys know a little bit of your trigonometry; that is u into cosine theta, so it is less.

So, what we have here is a triangle with this being d, this being a and this being theta; so this length is d square minus a square. So, cosine theta is nothing but root of d square minus a square over d; so I get energy that is useful is actually half mu u relative square; which is nothing but half mu u square into d square minus a square by d square. So, this is my incident energy epsilon T into 1 minus a square by d square.

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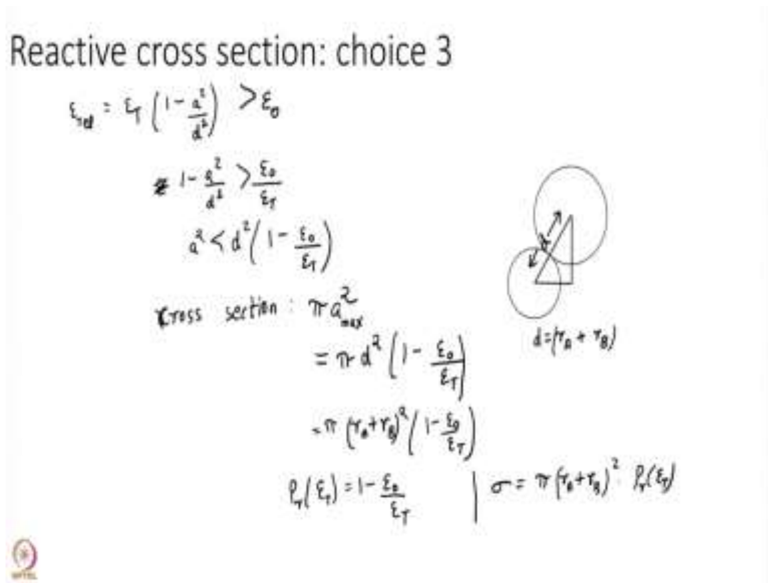

So, I have this epsilon relative equal to epsilon T 1 minus d square over a square of 1 minus a square over d square, my apologies. And we want this relative velocity to be greater than epsilon naught. For this relative velocity that I am putting in must suffice some activation energy for the reaction to happen; that is a much more natural choice to make.

So, this let me simplify I will have 1 minus should be greater than epsilon naught over epsilon T. I will just juggle around a little bit and I will get a sorry, a square to be less than d square into 1 minus epsilon naught over epsilon T. So, this is pretty easy to just manipulate around hope you can do that. Now, reactive cross section is really pi a square, pi a max square; so the maximum a for which the reaction will happen.

But, that will be equal to then pi d square into 1 minus epsilon naught over epsilon T. But, remember what was d was this, and d is equal to rA plus rB; so I have pi rA plus rB square. So, essentially what I get is Pr of epsilon T is 1 minus epsilon naught over epsilon T; so remember that sigma equal to pi rA plus rB square into Pr of epsilon T. That is what we proved two or three slides above.

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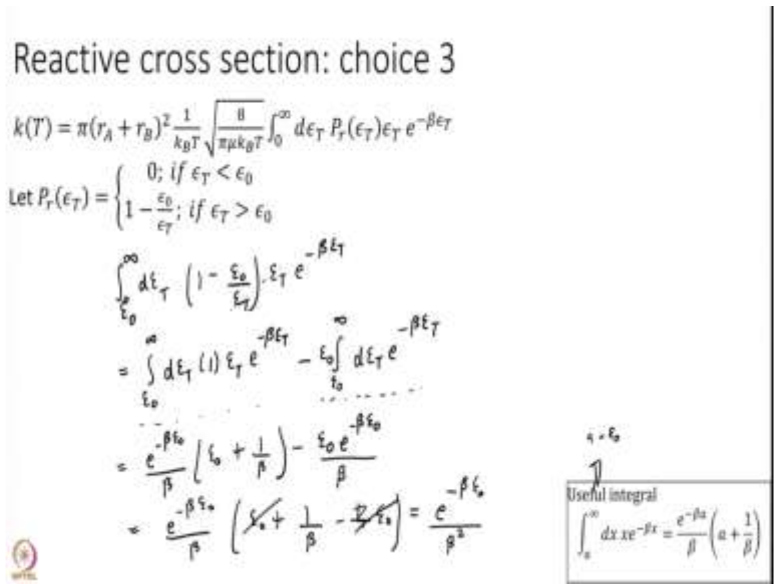

So, we get now this equation this choice that Pr is 1 minus epsilon naught over epsilon T, if epsilon is greater than epsilon or not; and if it is less than epsilon then no reaction will happen. So, now we will do this integral 0 to infinity, I better start with epsilon naught to infinity; because 0 to E naught will be 0, just like we did in the last case, last choice.

d epsilon T 1 minus epsilon naught over epsilon T epsilon T e to the power minus beta epsilon T; this becomes equal to two integrals. Integral over 1 I am just opening the bracket minus in the second one you will notice that this will cancel with this. So, I will have epsilon naught, d epsilon T; well this integral we have already done. And this is equal to basically I will again use this with a equal to epsilon naught.

I will have e to the power minus beta epsilon naught over beta, epsilon naught plus 1 over beta minus epsilon naught. And this integral you can do comes out to be e to the power of minus beta epsilon naught divided by beta. So, I go ahead and do this integral on your own it is not very hard. So, what I noticed is I take this to be a constant and you noticed this cancels; so this becomes equal to e to the power minus beta epsilon naught over beta square.

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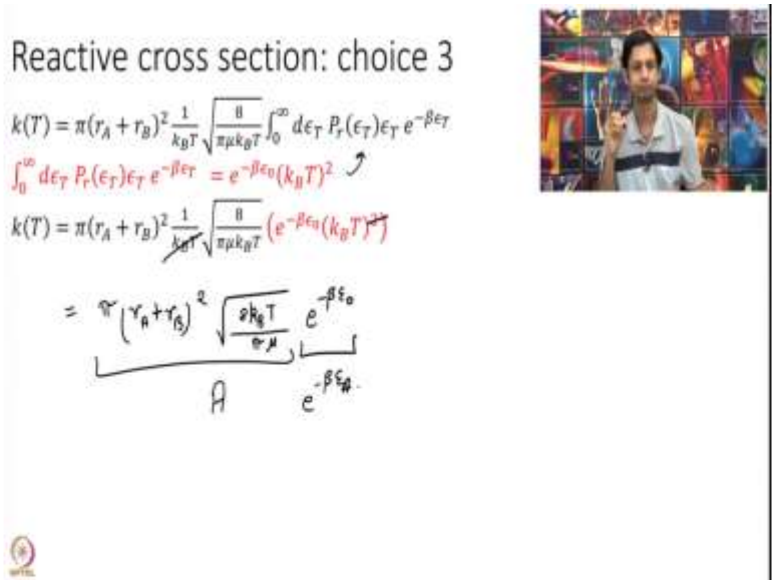

So, I have just replaced that a question here and put it back into this integral to get this. And so now you see what happens something very beautiful; which is what Arrhenius equation looks like. So, this is your Arrhenius factor and this is your pre exponent.

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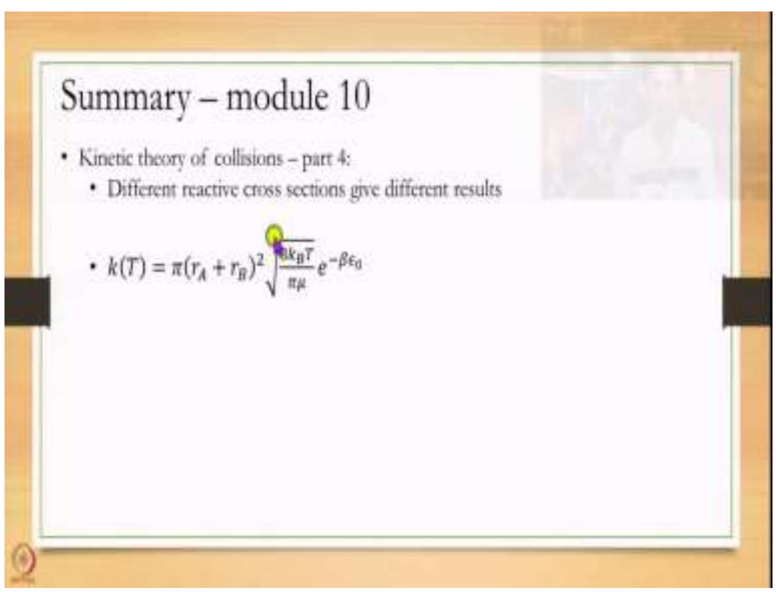

So, in summary today we have looked at different reactive cross sections and defined a reactive cross section. Reactive cross section again is the area in which B has to be in such that the reaction will happen. And if I do my math and calculate the reactive cross section and put a condition that the reaction will happen, only if the energy is above e naught. Then I can derive the Arrhenius equation out, given by this term here. In the next module we will see how we can use this to solve our problems actually. Thank you very much.