Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 44
Reaction dynamics - Part 7

So, we are now going to implement or this energy criteria very cleverly.

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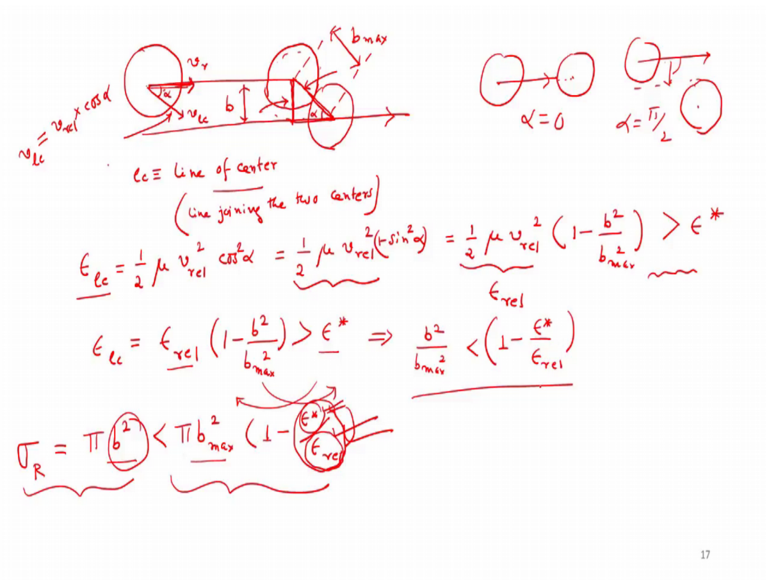

Now, think about it that as before we will say that one particular molecule is moving which is the m molecule or b molecule does not matter and there is a second molecule which is sitting here and when it comes here. So, this guy is suppose moving and this is static and when it comes here it will be something like this.

So, there will be a collision let me just draw it slightly in a bigger way something like this and this is basically the center of the second molecule which is static because we are talking about relative velocities. Now, the question is we need to make this impact how much energy actually is transferred in a bad drawing this is just ok. So, the question is how much energy is transferred along this line of center that is more important.

So, if you have a head on collision. So, all the energies are transferred along the line which is joining the centers, but here if we have a slightly off center. So, then all the energies will not be transferred only the part of the energy will be transferred. So, that we have to calculate now how to calculate that for that we are saying that fine, there is a v relative along this direction and suppose, it is making an angle alpha with respect to the second molecule and which means that along if this is alpha the component of the velocity along this will be nothing, but.

So, these are calling as v l c; l c means it is basically line of center. So, v l c means actually the component of the velocity along the line of center means the line joining the two centers line up center means line joining the two centers.

So, they are actually the energy will be transferred. So, we are writing in terms of velocity, but we can easily convert it to energy that we already know and then we can ask this question, fine, what will be the energy transferred along this line of center and that will be nothing, but half m v square, but instead of m, we have to write mu because it is a reduced mass system.

So, only one particle is moving other one is static and then we have to write the v relative now you see here. So, this is the v relative. So, the component along this line of center will be nothing, but. So, this v l c which is nothing but v relative into cos alpha so, this will be v relative square into cos square alpha.

Now, cos square alpha I can easily write it as v relative square I can write it as sine square alpha. Now, the sine square alpha; now the question is how will I write it. Now think about it if I just ask; what is this distance this distance is nothing, but r a plus r b; the joining line of the two centres.

So, this is nothing, but b max and this I am calling as b. So, b is our variable b is the basically center to center parallel distance, but then that b can be a maximum to b max. So, if this b max you can see from this triangle you can easily see this triangle. So, this thing is b max this thing is b and this angle is alpha.

So, I can easily say what is sine alpha sine alpha will be nothing, but b by b max. So, sine square alpha instead of that I am writing as v relatives square into. So sorry, it will be 1 minus sine square alpha 1 minus b by b max.

So, it will be b square by b max square. So, that is basically the energy transferred along the line of center that should be greater than some threshold energy otherwise the reaction will not happen that we are making an condition and that is why you are imposing it, fine, let us assume that this energy transferred along the line of center should be more than epsilon star which is the threshold energy.

Now, we have done a very simple calculation here that alpha can be 0 for head on collision as you can see and then for grazing collision that alpha will be 90 degree, if you remember, this head on collision means this is just directly coming and the same the second particle center is also like that there alpha is 0 and the other extreme could be this particle is moving and the second particle is just lying here.

So, this alpha in this case is 90 degrees or pi by 2. So, varying the b means actually varying the alpha, but we are just using the b language they are all connected now the question is so earlier; we saw that this pi b max square.

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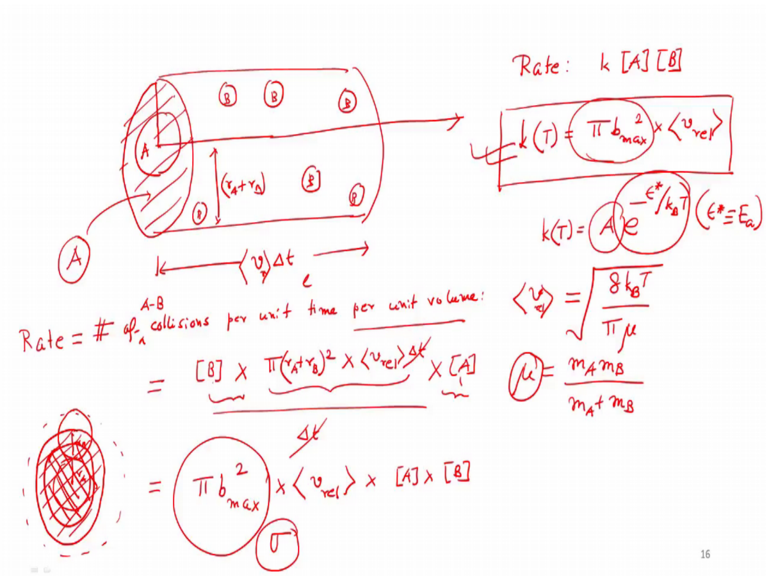

It has a dimension of cross section because if you think that what we what is b max? There is one molecule which is suppose hitting another molecule which is bigger molecule or smaller molecule.

So, we can think of these are the two molecules and we said that one is say r A 1 is r B r A plus always b max and we said that if you think of this cross sectional area. So, within this area whichever molecules center will lie within this area those molecules will be hit by the molecule which is actually moving at the center.

So, this molecule is moving around it; it has a own cross sectional area. So, that area is nothing, but pi b max square that area since it is a value of dimension of area. So, we call it as sigma. So, pi b max square sometimes its written as sigma, but right, now, we made an criteria that this sigma has to be greater or equal to something so, that we will see.

So, this sigma is nothing, but pi b square or before we go to the definition of sigma. Let us just look at only this part. So, this part basically tells that I have half mu before we proceed this half mu v relative this thing this also is dimension of energy because half m v square is a kinetic energy. So, instead of half mu v relative we could write it is basically the relative kinetic energy.

So, what I got is these line of control the energy transferred along the line of control should be its like this 1 minus b square by b max squared and that should be greater than epsilon star or we can just rearrange it, you can say that you can easily figure out that these b square by b max squared should be less than equal to 1 minus epsilon star by epsilon relative you can easily figure out to that.

So, you could just put this epsilon relative here and then bring this back here and this and bring this b max in other side, you can easily figure it is the length less than sign. Now this is the criteria. So, what it means is that think about it. So, we can just write it in other way, like you can just write it as or let me just use this path. So, what I am saying here b square has to be less than b max squared into 1 minus epsilon star by epsilon relative.

So, think about it like this b square if the epsilon star is 0 which means actually there is no activation energy, then it will be check all the criteria we have is just this b star will be will just have to be less than b has to be just less than B max.

So, any collision will give me the reaction. So, b goes from 0 to up to b max and all this coalition will give me reaction; however, if we make this choice that no actually, there is an epsilon star which is actually a pretty high affinity nonzero value of course, you have to have a criteria that epsilon relative a reality of energy.

If this is less than epsilon star, then no reaction will happen because think about it, if then actually, this will be this factor will be more than 1 and then actually, it will be a negative number which makes it does not make sense because what I am going to do is that I am going to multiply both sides by pi which is an area, but then area is becoming negative which does not make sense.

So, those reactions will not happen. So, epsilon relative has to be greater than epsilon star now if epsilon star has value, then it says fine suppose it is epsilon star by epsilon relative is 0.5, then I will get 1 minus 0.5 is 0.5 and then what I am saying is that this reaction probability is not exactly the cross section is not the exactly pi B max; it is slightly less than the pi B max, it is half of that area which means that the in the earlier case what we are saying that there is a effective cross section that we already wrote and all the collisions if they heat it then the cross section will be nothing.

But pi b max squared; however, we are now saying that no, no, all cross sections will not give you a reaction only a fraction of this cross section will give me a reaction which fractions say for example, only this area which you are drawing like this a smaller area is giving me a reaction that the smaller thing is coming from this factor right now.

So, very cleverly change the cross section have reduced a cross section in the that only those reactions will be possible if it is a less than say particular the relative energy is more than the epsilon star now suppose to be epsilon you look if energy is just equal to epsilon star. So, this factor will be 1. So, 1 minus 1 will be 0.

So, that cross section we are seeing is 0. So, we are saying that only the head on collisions will give me reactions that is the meaning of that. So, this cross section we are calling is an and the reactive cross section this is not simply pi b max square it is pi b square, but this b square is now connected I mean it has a criteria that it has to be less than equal to that.

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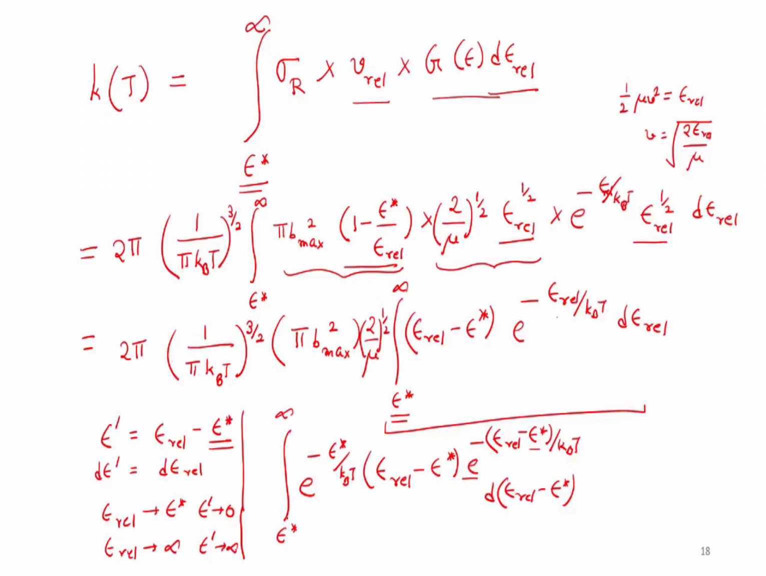

So, the reaction probability will be nothing, but now the rate will be thermally averaged rate constant will be nothing but this reactive cross section as we have seen times the relative velocity and then we have to take the average.

But we have not taken average on relative velocity because we do the averaging now and then we are basically saying, fine and let us take an average over all the basically we are integrating and we are saying that all these energies will give me a reaction that will be the total rate constant; however, only when this relative energy has a minimum value of epsilon star and it is going to infinity.

So, that integral just we have to solve right now. So, we know that this sigma r is nothing, but pi b max squared as you can see here where is it is here pi b max squared into 1 minus epsilon star by epsilon relative and then it is multiplied by v relative, but I cannot write v relative because I am integrating in the energy friend.

So, we can easily say that you already know this thing it is a half mu v square is epsilon relative. So, v is nothing, but twice epsilon relative divided by mu and square root of that. So, you will write it is twice epsilon relative or we write it slightly differently two by mu square root of that and epsilon relative to the power half and then I have g epsilon d epsilon which is the distribution function.

So, this is basically sigma r this is the relative velocity expression and then I have if you remember this distribution which we just got this distribution. So, it is 2 pi 1 by pi K B T raised to 3 by 2 e to the power minus epsilon by K B T epsilon to the power half d epsilon.

So, what is write it. So, it is nothing, but there are some constant we can write it at the beginning 2 pi times 1 by pi K B T raised to the power 3 by 2 and then e to the power minus epsilon by K B T epsilon to the power half these are all relative epsilon d epsilon. So, that is the expression for g epsilon d epsilon.

So, let us now calculate it. So, the lower limit is epsilon star the upper limit is infinity, now see this look at this integral very carefully. So, what do you have is pi b max square, but that is also constant that we can also take it out of the integral. So, 2 pi 1 by pi K B T raised to the power 3 by 2 into pi b max squared inside integral, let us see this I can write it as epsilon relative minus epsilon star divided by epsilon relative, but then I also have one epsilon relative to the power half and epsilon relative to the power half those will give me epsilon relative.

So, that will cancel with this epsilon relative. So, I am not writing that and then I have two by mu square root of that and inside; I have e to the power minus epsilon this should be epsilon relative because I am writing the distribution function also in the relative coordinate by K B T d epsilon relative.

Now, we have to somehow use the gamma function, but we cannot use because the long limit is epsilon star and also the variable here is epsilon relative. Now, we can make a trick we write it, fine, let us say that I just write it a new parameter which is epsilon prime which is basically epsilon relative minus epsilon star.

So, then d epsilon prime will be nothing, but d epsilon relative why because this is a constant this is a particular fixed energy above which this reaction is happening. So, this integration I can just rewrite only this integral part I am not writing the in between whatever we had. So, that I can write very cleverly as e relative minus epsilon star times e to the power minus e relative minus e star into d e relative.

So, basically I am writing it as de relative minus e star because we know that d epsilon star is this is nothing, but d epsilon star which is the epsilon relative is the same, but now look at it what I have done in this process I have actually multiplied this as extra factor which is e to the power plus epsilon star by K B T I put it inside a bracket.

So, then which means that is why it is a minus sign; so, I have to also multiply by e to the power minus epsilon star by K B T; then I can integrate it, this is the value of the this is the integration and then I can actually switch to epsilon star and we know that if e relative the lower limit is epsilon star then epsilon prime actually goes to 0.

So, in that relative thing; if I just write it then the lower limit will be now 0 in the next step and when e relative goes to infinity epsilon prime also goes to infinity.

Now, I have actually 0 to infinity limit and then I can write as integral once again.

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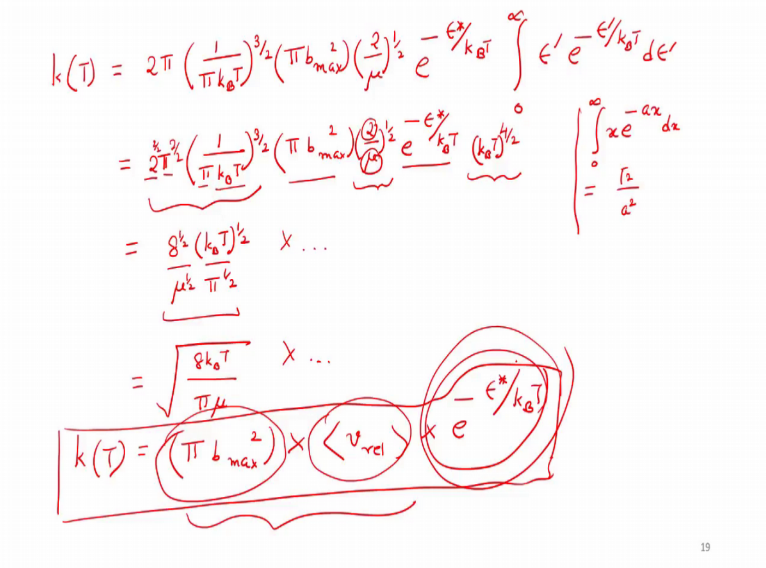

So, K B T will be nothing, but let us first write a constant all these constants. So, it will be 2 pi times 1 by pi K B T raised to the power 3 by 2, then I have pi b max square times 2 by mu square root of that and then let us see, now this factor is a constant because epsilon star is also a constant. So, I will have e to the power minus epsilon star by K B T into integral; I am now writing the variable as epsilon prime.

So, I can write it as epsilon relative minus epsilon the star, I can write it as epsilon prime sorry epsilon prime and e to the power minus epsilon prime by K B T d epsilon prime and the limits will be now 0 to infinity. Now, this is an gamma function of the form of x e to the power minus a x d x that we can easily follow it. So, it is x to the power n minus 1.

So, x is nothing, but x to the power 2 minus 1 x to the power 1 is x to the power 2 minus 1.

So, it will be gamma 2 by a to the power two and here a is 1 by K B T remember. So, the problem of the integral will be gamma 2 is nothing, but 1 gamma 1 which is just one and it will be just s square. So, we can right away evaluate. So, it is 2 pi 1 by pi K B T raised to the power 3 by 2, then I have pi b max squared 2 by mu to the power half e to the power minus epsilon star by K B T times this value of this integral will be it is 1 over a to the power a square.

So, the a was 1 by K B T that squared. So, it is nothing, but K B T squared it will be K B T squared. Now, let us simplify what do we have. So, what you can see here we have 2 here; 2 to the power of half and let us work out with 1 by 1. So, this term and this term I will not touch, I will just arrange with all other things. So, what we are getting K B T square and here K B T and the denominator to the power 3 by 2. So, the square thing we can think of as it is 4 by 2.

So, I will have K B T to the power half and then think about the pie. Now, I have a pie here I have a pie here. So, I am not touching the pie b max square. So, that will just keep intact. So, pi is basically it is pi to the power 2 by 2 and this is pi to the power 3 by 2.

So, I will have in the denominator pi to the power 1 2, then I have 2 here, I have 2 here. So, 2 means actually 2 to the power 2 by 2 and it is 2 to the power 1 by 2. So, I will have 2 to the power 3 by 2 which is nothing, but 8 to the power half. So, because 2 cube is 8 and then I also have a mu here.

So, I have basically mu to the power half. So, this thing is nothing, but 8 K B T by pi mu which is nothing, but v relative average. So, what we get? So, all these terms actually rearrange to give you v relative average and what we get is pi b max squared times v relative average I did not write all the other terms and times I will have e to the power minus epsilon star by K B T.

So, now this is a modified expression for the rate constant and we see the beauty here. So, the earlier expression had only this part by b max square into v relative and now we have actually e to the power minus epsilon star by K B T. Now this is a very beautiful result because we what do we what we exactly was looking for we got it because it shows that in a slight behavior and we got it from just by using the fact that this impact parameter; it is connecting to the impact parameter that this ratio of this impact parameter to the maximum impact parameter will actually be connected to this threshold energy and from that we got that; fine.

This we got back by the way the old cross section which is the overall cross section and then mean there is a primitive velocity, but then it is saying that fine. So, all collisions will probably happen grazing to head on collision.

However, with a condition that all the conditions are now here sitting here in that Boltzmann factor that the energy has to be above our threshold energy which is epsilon star does we see that even a very simple model which is the collision theory model that gives a very much Arrhenius like expression which we got.

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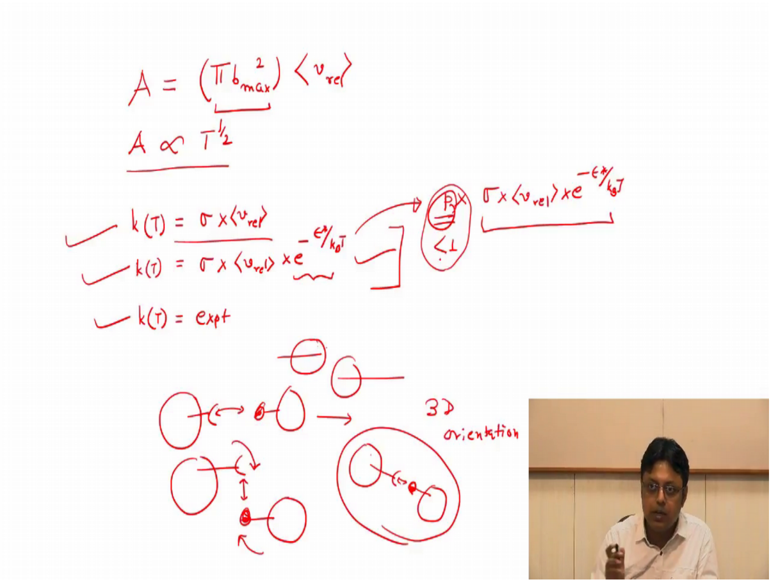

And then this simple collision model which we did not get where we did not impose the energy criteria.

So, A is nothing, but your pi b max squared into v relative average. Now, you see that it has a temperature dependence because v relative goes as square root of temperature. So, the temperature dependence is not only coming from the exponential part it is also there. So, the pre exponential factor is also temperature dependent now when you calculate or when you give you some problems experiment we asked to use this formula and calculate our rate constant for a reaction for which actually you already know that it constant we using the three values.

So, you can actually first get at our old collision theory which is nothing, but this sigma if we call these as A sigma and times the v relative and this is the old thing and this the modified thing we got an expression like v relative into e to the power minus epsilon star by K B T. So, moment you include this factor you will see the number of collisions that give is giving their reaction you will be right.

So, the rate constant which you calculate using this formula will give you a very high number which is not a true number rate constant which you get which in this formula will be more close at work it will be a lower number which will be more close, but still the actual rate constant which you get experimentally will still be much lower than this calculated rate constant.

The reason is there is also an orientational factor that you did not discuss suppose; what do you mean by that suppose a collision is happening with some particular energy and we know that from this expression that this will be a reactive collision. However, these molecules are not hard sphere they also have particular structure and this particular atom should come closer together. So, by that what I mean suppose if this is perfectly oriented like say I have some group here and I have some group here.

So, if I have a head on collision these two will react together to give me a reaction, but suppose now I am having a collision like this and then although these two hard spheres collide the these two groups are not actually coming in contact with each other; however, if I had rotated it and rotated it in the sense that they are still colliding and they are also they are slightly far apart, but when they collide they actually these two group will come in contact and then reaction will happen.

So, then it means that the proper orientation is also very important or the three dimensional orientation is very orientation is very very important. So, people actually to get to current or get a better experiment or better result sometimes they just write this is compared these two values and they write it fine actually we will get the true value.

If we multiply it with some other factor which is sometimes called p which is known as probability factor times this modified rate constant which is sigma into v relative into e to the power minus epsilon star by K B T and this probability factor will always be less than 1.

If it happens that these molecules are actually behaving like hard spheres in this probability factor is equal to 1 and whatever we just derived that expression is perfect, but in reality actually molecules are particular chef and this reactive ends has to come closer together through a proper orientation then actually the rate constant which you are calculating is giving you an upper limit.

So, the actual rate constant will be slightly lowered. So, it will be not only that is collision with a particular energy, but also it needs the right orientation and that orientation you can I mean compared with the experimental value and you will find that there is also another factor which is less than 1 that actually will bring down the calculated rate constant to the experimentally observed rate constant.

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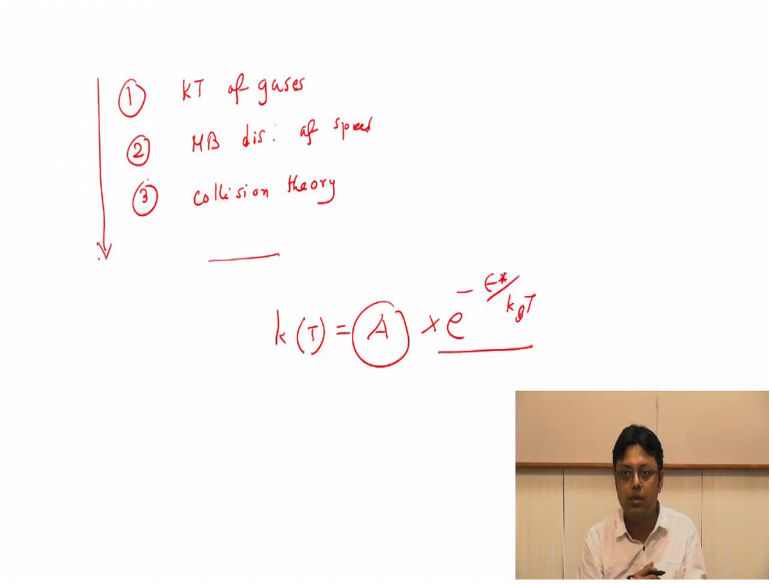

So, summarize actually what we discussed in this lecture is that we first talked about kinetic theory of gases and then we talked about in detail the Maxwell Boltzmann distribution of molecular speed and then we used it to give the expression for the rate constant by collision theory and we showed how basically one can use very cleverly the impact parameter and connected to the threshold energy to get Arrhenius like rate expression.

And we showed that we can actually calculate this A or the pre exponential factor in Arrhenius equation and we can get an expression where this thing also comes up and that was our entire goal in reaction dynamics which will short that by using all this development you can actually calculate the rate constant using just the classical mechanics.

Thank you.